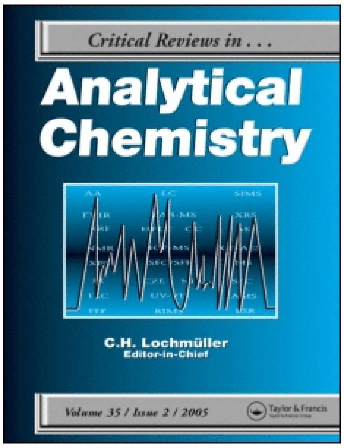


Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Atomic Spectrometric Analyses of Ferrous Materials

C. B. Belcher; Theodore C. Rains

To cite this Article Belcher, C. B. and Rains, Theodore C.(1978) 'Atomic Spectrometric Analyses of Ferrous Materials', Critical Reviews in Analytical Chemistry, 7: 2, 121 — 186

To link to this Article: DOI: 10.1080/10408347808542700

URL: http://dx.doi.org/10.1080/10408347808542700

ATOMIC SPECTROMETRIC ANALYSES OF FERROUS MATERIALS

Author: **C. B. Belcher**
Central Research Laboratories
The Broken Hill Proprietary Company Ltd.
Shortland, 2307, Australia

Referee: Theodore C. Rains
Analytical Chemistry Division
National Bureau of Standards
Washington, D.C.

TABLE OF CONTENTS

I. INTRODUCTION

The level of ferrous metallurgical extraction and refining activity is a significant indicator of the technological development of any nation. The 1975 world production of iron ore and steel was 881 and 636 million tons, respectively,[1,2] which by present-day monetary values would require a capital development investment of \$1 X 10^{12}. Many and various analytical techniques are being used to control ferrous metallurgical production.

Atomic absorption, emission, and fluorescence spectrometry have been increasingly used to meet the quality assurance requirements of the industry, and the current literature describes applications for 33 elements. The rapid emergence and wide popularity of the techniques lie in several of their advantages such as simplicity of operation, little influence of coexisting elements, ability to carry out successive determinations for many elements, and high sensitivity for many trace elements.[3] Of the three techniques, atomic absorption spectrometry (AAS) is most extensively used; however, atomic emission spectrometry (AES)[4,5] and atomic fluorescence spectrometry (AFS)[6,7] are being used for specific applications. Further developments in AES and AFS are being achieved. Atomic spectrometric methods have been used for the range of 0.01 to 300,000 μg/g,[8-10] with the best relative standard deviation being 0.1%.[11,12] The limits of detection (c_L)[13] can be improved by 1 to 2 orders of magnitude when preliminary separation, concentration, or evolution techniques are used with solution media.[14,15]

Quality assurance and research programs require interference-free methods which give a high level of precision, accuracy, and speed; atomic spectrometric methods are competitive on the first two points, and analysis times of 2, 5, and 10 min from sampling have been reported for anodic dissolution-flame AAS,[16] cathodic-sputtering AAS,[7] and graphite furnace atomic absorption spectrometry (GFAAS), respectively.[17] The continued development of ferrous alloys has placed increased emphasis on the deliberate addition of minor elements in small but carefully controlled amounts, a numerical increase in the elements used to make specific alloys, and lowered maximum specification limits (as low as 0.5 μg/g) for deleterious residual elements. The smooth operation of large blast furnaces with increased emphasis on environmental considerations, has necessitated the control of SiO_2/Al_2O_3 ratios and numerous minor elements in iron ores.[18] Accordingly, the majority of ferrous metallurgical laboratories use an atomic absorption spectrometer, often with emission or fluorescence attachments, to assist control and development programs.[19]

The usage role of these atomic spectrometric techniques varies according to the size or production requirements of a laboratory. For major iron ore or steel laboratories, rapid quality control is generally provided with X-ray fluorescence spectrometry (XRFS) and/or optical emission spectrometry (OES); these techniques provide simultaneous multielement analyses with an elapsed time of less than 1 min. However, multichannel spectrometers require a wide variety of standard samples, the majority of which are not available from recognized agencies. Accordingly, atomic spectrometry provides a preferred method of analysis for many elements.[20] Previously, these requirements were mainly satisfied by gravimetric, volumetric, molecular spectrometric, and polarographic techniques. Also, a significant number of samples are presented in a physical form unsuited to multichannel spectrometers, and, in these circumstances, atomic spectrometric methods are ideal; indeed, a 1-g sample is often sufficient for the analysis of some 10 to 20 elements.[3,10,21] Also, the analyte or concentration level may be unsuited to multichannel spectrometric procedures, and, again, atomic spectrometry often provides an attractive method of obtaining the information sought. For smaller laboratories, where a longer elapsed time for receipt of analyses may be tolerated, atomic spectrometry provides quality assurance with significantly lower capital and operating costs. For research laboratories, atomic spectrometric techniques often provide the only practical means of obtaining a result.

Progressive advancements are being made in the electronic logic and design of new atomic absorption spectrometers. Particular attention has been paid to microprocessor control, automation of sample presentation, correction of calibration curve deviations from linearity, direct concentration readout, automatic printout of results, and improved reproducibility. The majority of spectrometers can be converted to atomic emission and fluorescence modes.

Further significant advances are being made in signal processing and sophistication of attach ments, such as automated hydride generators and graphite furnace (GF) atomization devices. The budget price for a complete spectrometer can vary from $10,000 to $40,000 which at the middle to higher end represents a substantial investment for a single- or, at most, a double-channel spectrometer. This review provides background information which should aid in the decision-making process in the purchase of atomic spectrometric equipment for ferrous metallurgical analyses.

II. SCOPE AND ORGANIZATION OF REVIEW

This review considers ferrous materials to be metals, alloys, oxides, and intermetallics which contain more than 50 mass% iron. The major classes of ferrous materials within this definition are iron, steel, and iron ore. The terms low and high alloy are used to describe metallics with > 95 and 50 to 95 mass% iron, respectively.

Multichannel techniques and applications are not included in this review. However, techniques considered include those which improve the precision and accuracy of atomic spectrometric methods by using either a second channel or monochromator, repetitive optical scanning,[22] or a double-beam monochromator to monitor such parameters as an internal standard,[5] background,[12,23] or light-source fluctuation.[7]

The application of AAS, AES, and AFS for the determination of 23 elements in ferrous metals and alloys from 1961 to 1970 has been comprehensively reviewed.[24] Accordingly, the present review covers developments from 1970 to 1976, although, in a number of instances, information has been extracted from earlier literature in order to present a comprehensive viewpoint. This review is more descriptive of the relatively newer techniques which have been proposed.

The majority of experimentation and application efforts has been directed toward the AAS techniques. However, similarities of sample preparation and instrumentation suggest that the minor-used techniques of AES and AFS should be reviewed simultaneously. This decision creates some difficulty in deciding the sequential arrangement of the various sections of the review, which has been resolved by allocating successive sections to standards, analyte atomization techniques, sample dissolution and preparation techniques, and illustrative examples of the determination of specific elements. This arrangement emphasizes problems, observations, and developments which, in many instances, are common to all three techniques.

Adequate reviews of theory and general instrumentation appear on a regular basis and are not discussed. Commercially available apparatus is not reviewed in detail other than to emphasize a desirable feature or to demonstrate shortcomings.

III. STANDARDS

The American Society for Testing and Materials (ASTM) published a set of recommended practices for AAS[25] in 1971. While some of the instrumental concepts have been superseded, the document provides an excellent outline of successful sample preparation, separation or preconcentration techniques, analyte losses, and contamination. The Standards Association of Australia (SAA) published a code of practice particularly useful for defining the conditions required to obtain the highest precision and accuracy[26] for AAS. This code is being revised. The ASTM has published suggested practices for flame AES methods of analysis, embodying an extensive outline of principles, practices, and instrumentation.[27] The present lack of a standard code of practice for the newer electrothermal atomization technique is a matter of concern.

The rapid development of atomic spectrometric techniques has disclosed shortcomings in available materials and apparatus. Analytical chemists are able to develop experimental conditions which, when used by another chemist in another laboratory, often fail to give satisfactory results. The solutions to these difficulties lie in continual exchange of experience, improved standard reference and pure materials, and the codification of minimum specifications for instrumentation. Atomic spectrometric techniques as applied to ferrous material have disclosed difficulties which require improvement. The four significant areas (standard methods, instrumentation standards, standard reference materials, and calibration standards) are discussed in the following subsections.

A. Standard Methods

The small number of published standard methods is disappointing. The Japanese Standards

Association (JSA) has published AAS methods for the determination of 17 analytes in iron and steel[21] and 15 in iron ore.[28] This fine effort was achieved through active investigations by the Chemical Analysis Subcommittee of the Iron & Steel Analysis Committee in the Joint Research Society of the Iron & Steel Institute of Japan.[3] The recommended iron ore methods have been translated into English.[29] The ASTM has published four AAS methods: lead in alloy steel,[30-32] magnesium in iron,[33] and aluminum,[34] calcium,[35] and magnesium[35] in iron ore. The SAA has published six AAS methods: lead[36] and cobalt[37] in steel, magnesium[38] in iron, and aluminum,[39] calcium,[40] magnesium,[40] and manganese[41] in iron ore. The International Organization for Standardization (ISO) and the British Standards Institution have not published any standard methods in the fields being reviewed, although some drafts have reached an advanced stage. Standard methods have not been published for AES or AFS.

Endo[3] discussed the significant progress made by the JSA and emphasized the attractiveness of AAS for successive determinations and the substantial impact achieved in the field of iron ore analysis. Of 21 elements significant in iron ore, 15 can be determined by flame AAS without preliminary separation or concentration. The six elements for which AAS was not applicable were Fe and Si (the concentrations being too high) and As, Sn, P, and S (the maximum impurity limit being incompatible with the sensitivity).[13] The reviewer feels that sufficient development has taken place since formulation of this standard[28] to allow the determination of Si by flame AAS and As and Sn by electrothermal atomization or hydride evolution. JSA standards permit burner rotation to optimize concentration ranges and absorbance; however, this procedure is not compatible with obtaining the best accuracy with minimum freedom from interferences.

British workers have examined flame AAS methods (Al, Co, Cr, Cu, Mo, Ni, Pb, and V in steel) which could form the basis for producing standard methods.[42] The nine cooperating laboratories used seven different models of atomic spectrometers manufactured in the U.S., United Kingdom, or Australia. Satisfactory results were obtained for all elements (excepting chromium); this is in accord with the experience of many workers. Ottaway[19] felt that some improvement could be achieved by more careful optimization of the working conditions. The difficulties experienced have been mainly attributed to differences in flame characteristics between the commercial instrumentation used,[19,42,43] e.g., the laboratories which had positive biases using the lower temperature air-C_2H_2 flame were also biased high with the higher temperature N_2O-C_2H_2 flame even though differing matrix and solution media were used for each investigation;[19] the extent of bias was noticeably higher with alloy steels.[42] There were significant differences between the appearance characteristics of the "red feather" of the N_2O-C_2H_2 flames required to obtain the correct result in each laboratory.[42]

Ottaway,[43] when developing an AAS method for chromium in steel, found no interference effects when using a tall (11-mm optimum optical path height) 50-mm long air-C_2H_2 single-slot flame with fairly well-defined zones, whereas serious interference effects were encountered with an alternative 100-mm long air-C_2H_2 single-slot flame with a smaller (6-mm optimum optical path height) flame height and ill-defined zones. A similar trend was noted by Scholes[44] who edited a collaborative study of interelement interference effects experienced when determining aluminum and chromium in iron and steel by flame AAS. Seven different models of atomic spectrometers were used in the study, and there were wide variations in the degree of interference noted. It was evident that interference effects must be measured in each individual environment and that published works can only be used as a guide.

It has been quite correctly concluded that when standard methods are being developed, several manufacturers' units should be included in the development and validation programs.[19] The bias and interference patterns observed in the various collaborative studies should be critically examined, so that the slot width and length and gas pressures and flow rates could be more closely specified for future apparatus design. Such observational evidence could also provide a concrete basis for mandatory specifications to be included in a standard method.

Many difficulties encountered during collaborative studies aimed at developing standard methods could be avoided if workers would appreciate that flame conditions giving the best sensitivity are often not optimal for freedom from interference.[45,46] Ottaway[19,47] showed that there is, a relationship between increasing fuel richness and the commencement and progressive development of interferences caused by aluminum, iron, and titanium when determining chromium in steel by AAS. The reviewer concludes that an interference-free method could have been developed (with poorer sensitivity) by using a flame condition free of interference from all three potentially interfering elements.

Another approach recommended for certain situations is that adopted by SAA for the determination of cobalt in iron and steel. The method[37] recognizes that with certain flame conditions, interferences can be avoided by not using maximal sensitivity; acknowledges that the interfering elements are iron, nickel, and chromium; and invites the analytical chemist to select the flame condition which gives similar absorbance readings for two calibration standards, both containing the maximum recommended cobalt concentration, with significant varying concentrations of the potential interfering elements. This approach has the additional advantage that the potential interferences experienced in each laboratory and the differing degrees of interference between laboratories can be avoided. The adoption of this technique where necessary would increase the publication rate of standard methods.

Another significant deterrent to the formulation of standard methods is the failure to use rigorous sample dissolution techniques. Cobb et al.[42] propose a standard method using only hydrochloric acid as solvent which did not fully dissolve the sample and removes the silica containing the encapsulated and absorbed analytes. The lack of suitable complex standard reference materials or use of those with inadequate or nonexistent results for the analyte element often camouflages the inadequacy of proposed sample preparation methods.

In summary, increased production of standard methods seems to be dependent upon the recognition and standardization of critical instrumental parameters, a more rigorous approach to sample dissolution, a willingness to define flame conditions which can be reproduced between laboratories, and improved availability of standard reference materials.

B. Instrumentation Standards

The majority of atomic absorption and emission spectrometers have been commercially manufactured, and the rapid development of analyte atomization techniques has obscured a number of unsatisfactory design features and has hindered the production of standard methods (Section III.A). In 1973, the ASTM[34,35] made a significant advance by publishing specifications for the sensitivity, curve linearity, and stability of atomic absorption spectrometers. Undoubtedly, these specifications can be tightened and others added when further experience is obtained, older spectrometers are replaced, and manufacturers react to developments. The SAA[37,39-41] and ISO[48] have followed the ASTM, and certain refinements of the specifications have been achieved.

For the AAS determination of aluminum in iron ore using 396.2 nm and a N_2O-C_2H_2 flame, ASTM selects a minimum absorbance of 0.3 for the highest calibration standard in the series.[34] This sensitivity is equivalent to 1.8 μg/ml 1% absorbance (A) for a standard containing 125 μg/ml in a media of 5% (v/v) HCl in the presence of 3 mg/ml Fe and 2.3 mg/ml Na. When this specification is considered in conjunction with curve linearity, the majority of present-day spectrometers should be adequate. Similar sensitivity specifications have been set for the determination of aluminum,[39,48] calcium,[35,40] magnesium,[35,40] manganese[41] in iron ore and cobalt in steel.[37] Undoubtedly, these specifications are necessary if consideration is given to a report by Scholes[44] on a collaborative study of the AAS determination of aluminum in steel using a 10 mg/ml iron media where nine participating laboratories (using seven differnet models of spectrometers) reported sensitivities from 0.6 to 4.3 μg/ml (1% A) when calculated from the absorption of the highest calibration standard.

ASTM selects a concentration limiting the extent of curve nonlinearity for the AAS determination of aluminum in iron ore.[34] The difference between the absorbance readings of the two highest calibration solutions (100 and 125 μg/ml, Δ 25 μg/ml) must be more than 1.4 times the difference between the absorbance reading for the zero and next lowest calibration solutions (0 and 12.5 μg/ml, Δ 12.5 μg/ml). A similar specification appears in a later SAA method.[39] Clarity has been improved in a similar ISO draft document as follows: the slope of the calibration curve covering the top 20% concentration range (expressed as a change in absorbance) shall not be less than 0.7 of the value of the slope for the bottom 20% concentration range determined in the same manner.[48]

The latter ISO draft specification[48] does not specify the top standard concentration, and, accordingly, the analytical chemist is allowed more initiative in assuring the best instrumental performance of a spectrometer. Ideally, the linearity specification should be tighter, but this depends on the experiences of various workers when comparing the means, biases, and precision within and between laboratories for collaborative results calculated from the upper half of calibration curves. This ISO specification, when considered in conjunction with the sensitivity specification, allows the user greater flexibility in deciding whether observations surpass the performance specifications of a standard method, thereby allowing further benefits to be achieved. Thus, the first ASTM standard AAS method[33] is overly restrictive upon the freedom of the user, is cumbersome, and uses floating sample weights and acid additions according to the sensitivity for each individual spectrometer.

ASTM states that the relative standard deviation (S_r)[13] values of a number of measurements of the highest and zero calibration solutions must be less than 1.5 and 0.5% respectively, when calculated with respect to the highest calibration solution.[34] Clarity has been improved by an ISO draft requiring that one standard deviation of the absorbances of the most concentrated and zero calibration solutions (each calculated from a sufficient number of repetitive measurements) shall be <1.5 and <0.5%, respectively, of the mean value of the absorbance of the most concentrated solution.[48]

Several limitations of commercial atomic spectrometers, when applied to GFAAS and GFAES, have been discussed.[4,49,50] The most significant problem is caused by excessive emission from the GF walls. Kerber et al.[49] have described the relative emission intensity, as a function of the wavelength for the inner graphite walls at 2200°C. Subsequently, significant improvements were made by using adjustable diaphragms, slit height modifications, and baffles on the monochromators; the longer term solution will involve a major redesign of monochromators. These improvements will benefit all techniques used in conjunction with AAS, AES, or AFS.

Previous workers have lowered N_2O-C_2H_2 flame temperatures by diluting the flame gases with argon or air in otherwise standard slot burners. These flames were used to optimize interference, suppression, or sensitivity when determining magnesium[51,52] and calcium[52] in ferrous alloys and iron ore.[35] Recently, Thompson and Godden[53] proposed the use of a wider slot burner head, 0.60 mm compared with the 0.43-mm slot normally used for higher temperature flames based on N_2O-C_2H_2. While this proposal was made in the specific context of pulse nebulization, the reviewer believes that the concept has a much wider appeal. The proposal requires the use of a continuous supply of inert gas, and, for the example quoted, a combination of 2 l/min N_2 and 11.5 l/min N_2O was required to avoid burner strike back. The comparative sensitivities (1% A), achieved with 5% (mass/vol) iron media, are shown in Table 1. The generally improved sensitivities achieved with the wider slot (0.60 mm) burner head are attributed to a larger flame volume, wherein the breakdown of refractory oxides can occur. The slightly poorer sensitivity experienced with silicon and titanium is not significant, particularly since other advantages were experienced: less susceptibility to blockage by more concentrated solutions was achieved, and the region of optimal burner height was not so critical. A good case has been made for the commercial availability and use of a relatively wider slot burner head designed to use a continuous supply of inert gas to give flame temperatures intermediate between the N_2O-C_2H_2 and air-C_2H_2 flames. This could answer the criticism leveled by Ottaway[19] against workers who chose the N_2O-C_2H_2 flame without adequate consideration of any disadvantages for a particular analyte. The disadvantage of providing controls for mixing of the inert gas with nitrous oxide is outweighed by the advantages achieved. An alternative would appear to be the use of premixed N_2-N_2O gas mixtures.

In summary, an improved instrumentation standard should flow from the introduction of specifications for the sensitivity, curve linearity, and overall stability of atomic spectrometers. Following detailed experience with collaborative studies tightened or further specifications may be required. A commercially available wider 0.60-mm slot burner head using a N_2-N_2O support gas with C_2H_2 could beneficially replace the more usual N_2O-C_2H_2 burner head for several analytes. Ad

TABLE 1

Comparative AAS Sensitivities of 0.43- and 0.60-mm Wide N_2O-C_2H_2 Burner Heads Using 5% (mass/vol) Iron Media

		Sensitivity (μg/ml/1% A)[a]		
		0.43-mm burner head		0.60-mm burner head,
Element	Wavelength (nm)	13.5 l/min N_2O	11.5 l/min N_2O + 2 l/min N_2	11.5 l/min N_2O + 2 l/min N_2
Al	309.3	1.0	1.2	0.75
As	193.7	1.7	1.5	1.1
Ba[b]	553.6	0.37	0.41	0.30
Si	251.6	2.0	3.5	2.1
Sn	286.3	2.6	2.4	1.9
Ti	364.3	1.9	3.5	2.1
V	318.4	1.5	1.8	1.3

[a] Samples continuously nebulized.
[b] Plus 1000 μg/ml K.

Extracted from Thompson, K. C. and Godden, R. G., *Analyst* (London), 101, 96 (1976). With permission.

ditional study of the potential is required. With GFAAS and GFAES techniques, improved baffling and adjustable diaphragms were required to reduce excessive stray light, indicating that a major redesign of monochromators is required to support the continued development of these techniques.

C. Standard Reference Materials

Standard reference materials are essential for establishing the validity of developed methods and providing a sound basis for the evaluation of precision and accuracy. The prediction that AAS would be interference free was not realized.[54] All three techniques being reviewed are subject to a variety of interferences, the effects having increased in severity as progress has been achieved in lowering the trace element levels which can be detected in ferrous metallurgical materials. In 1970, it could be stated with reasonable confidence that the ferrous metallurgical industry had been well served with adequate standard reference materials,[24] and more agencies have emerged to support the analyte range of 0.001 to 100%.

Rapid progress in ferrous metallurgical and environmental sciences has demanded analyses in the range of 0.01 to 10 μg/g, and atomic spectrometric methods have been forerunners in providing determinative techniques and methods to yield this information. However, the spontaneous progress achieved, particularly with hydride evolution and electrothermal atomization, has outstripped the availability of significant trace element information in standard reference materials.

Many method development problems are camouflaged by the absence of adequate trace element information on standard reference materials. These include:

1. The use of extremely simplified but inadequate dissolution techniques.
2. Sample preparation losses due to hydrolysis, volatilization, and entrapment are not revealed.
3. Many proposed methods are being verified at minimum concentration levels which are not less than two, three, or more decades higher than the apparent detection limit.
4. The calibration standards are inadequately matched, not given similar pretreatments as samples, or often contain the analyte element at a significant impurity level.

Selected illustrative examples are

1. Burke[55,56] could not present AAS data for 0.1 to 10 μg/g Ag and Tl.
2. Vasillaros[57] found available standards to be unsuitable for the determination of 1 to 10 μg/g Bi and Pb by AAS.
3. Fleming and Ide[58] could not validate the

majority of their work on the determination of hydride-forming elements.

4. Burke[59] developed procedures with an inherent c_L of 0.1 μg/g, but could only carry out limited validation at < 10 μg/g; subsequently, it was shown that bad or poor calibration curves had been obtained, and that the initially reported values, particularly < 10 μg/g had been in error.[60]

5. Ashy et al.[61] could not effectively demonstrate the application of the AAS induction-heated graphite well furnace technique to the determination of antimony in steel.

In summary, there is a very serious shortage of analyte information for standard reference materials of iron ore, steel, and iron for the range 0.01 to 10 μg/g. This shortage is having a serious effect on the sound development of proposed methods and newer techniques. The task of providing the required information may be too great for any one nation, and future needs may best be achieved by global cooperation among interested laboratories which can achieve the necessary determinations with the required c_L and relative standard deviation values.

D. Calibration Standards

Calibration standards represent the essential comparative interface between samples to be analyzed and the atomic spectrometric method used. The reviewer perceived far too many examples of inadequate matching of calibration standards and subsequent willingness of authors to discuss an entire range of observations and problems, the creation of which are due solely to faulty experimental design.

Atomic spectrometric techniques relying upon the presentation of a solid sample for analyte atomization depend entirely upon the availability of a suite of solid calibration standards. In many instances, it is not sufficient that the calibration samples be of the same chemical composition, but they also be prepared by the same production processes.[62] Standard reference materials from a national bureau are valuable for establishing preliminary working curves, identifying interferences, and determining precision; however, supplementation by secondary standard samples is essential.[62] The analyte atomization techniques of cathodic sputtering, aerosol generation, and furnace vaporization (described in Section IV.B) which depend exclusively on solid standard samples for the preparation of calibration curves are especially critical.

Again, the rapid development of hydride evolution and electrothermal atomization techniques has outstripped the commensurate availability of adequate high-purity materials suitable for the preparation of solution calibration standards. In 1970, metallic iron or ferric oxide with a total impurity limit of 10 μg/g and an actual certified analysis to the nearest 1 μg/g for all possible elements actually or potentially present would have been reasonably adequate for matrix matching of calibration standard solutions.[24] However, a number of atomic spectrometric techniques would now require reference iron with a total impurity limit of .1 μg/g and an actual certified analysis to the nearest 0.01 μg/g for some of the possible elements actually or potentially present. At the present time, material of this quality is not readily available, and the cost is prohibitive. Furthermore, workers should not use high-purity materials supplied without test certificates concerning stoichiometry and major element and actual impurity concentrations. It is essential that purchased high-purity materials be stored under very clean conditions and that contamination during use be avoided.

Against this background, it is difficult to understand how Thomerson and Price [10] would have difficulty in obtaining pure reference iron with sufficiently low levels of manganese and copper to enable analyses of these elements, at 0.02 and 0.01%, respectively. Also, Jacobson[63] found 10 μg/g copper in iron used for determining 10 to 2000 μg/g copper in steel by AAS; workers should preferably use pure iron containing the analyte at 1 decade of concentration lower than the c_L value (i.e., 1 μg/g Cu). Difficulty was experienced when determining 5 to 50 μg/g calcium in alloy steel by AAS due to 2 μg/g calcium in the iron used as calibration reference.[64] In this instance, iron containing < 0.5 μg/g calcium was not readily available; hence, the method of additions used to determine the calcium concentration of the iron avoided a result otherwise biased low by 2 μg/g. Although not mentioned in the literature, the reviewer cautions that vigilance is required to ensure that the concentration of the analyte be known or established for the minor matrix-matching materials other than iron, which are used for preparing solutions of calibration standards.

It has been emphasized that synthetic-base calibration standards should be similar in all respects to the samples being analyzed and that similar pretreatments be given.[3,26,65] Belcher[45] has stressed the necessity of having adequate knowledge of the iron concentration of materials being analyzed and advocates determination of iron content as a prerequisite to the preparation of adequate calibration standards. A recommended AAS method covers the range 50 to 100 mass% iron in a variety of commonly used acid media so that successive determinations of matrix and analyte can be achieved.[45] For some materials, it is necessary to determine matrix elements other than iron so that satisfactorily matched calibration standards can be prepared. Rooney and Pratt[66] noted that the interference effects of two or more elements in combination cannot be easily predicted from single element effects. In this regard, the reviewer suggests that particular attention should be given to any silicon allowed to remain in solution during sample preparation.

Thomerson and Price,[10,67] when determining chromium in steel by AAS, caution against the use of calibration solutions based on potassium dichromate because a progressively increasing concentration of potassium (a known ionization control agent) is added. The reviewer warns that it is a common mistake to add progressively increasing amounts of a nonanalyte or anion, which can exert an insidious suppression, enhancement, or ionization function. Common examples are the determination of silicon where the standard solution of silicon is usually prepared by fusion with an alkaline flux and the preparation of a standard solution in an acid dissimilar to the acids remaining after preparation of sample solutions for analysis. The problem can be avoided by choosing an element and flux/acid which will be compatible in every way with the solution of the sample or by making a substantial bulk addition of the hostile element/anion to achieve a plateau effect.

Some reported difficulties attributable to failure to completely match calibration standards and assays are

1. Headridge and Richardson,[68,69] when making AAS determinations of traces of bismuth via solvent extraction of bismuth iodide, produced calibration graphs indicating higher sensitivity if iron was not present in the solution media.
2. Ottaway[19] proposed the use of calibration standards without iron for the AAS determination of chromium; however, when the method was applied on a collaborative basis in six laboratories, depression of the signal by iron in the sample solutions was experienced in two laboratories.
3. Ottaway and Pradhan[43] used potassium dichromate (but no iron) to prepare a calibration series for the AAS determination of chromium in steel; however, it was found that the developed procedure was not applicable to another commercial atomic absorption spectrometer.
4. Burke[59] used organometallic standards when developing acid dissolution-solvent extraction procedures for the determination of 0.1 to 50 μg/g of deleterious elements in alloy steels; however, Thornton and Burke[60] subsequently discovered that the slope of the calibration curve based on the organometallic standards was lower than a curve carried entirely through the procedure using metallic standards.
5. Although Thomerson and Price[10] cautioned against the use of potassium dichromate to prepare standards for chromium determination, the use of potassium titanyl oxalate was suggested to prepare the titanium calibration in the same composite method.
6. Tugane et al.[64] experienced a variable interference effect from calcium extracted from filter paper when filtering solutions which were used for the AAS determination of 5 to 50 μg/g calcium in alloy steel, and it was recommended that the papers be washed with 10% (v/v) hydrochloric acid prior to use and that the calibration solutions be filtered similarly.

A related problem is illustrated by an ASTM method (1975) for aluminum in iron ore which proposes the use of 2.3 mg/ml sodium in calibration standards and only 1.2 mg/ml in the assays.[34] The sodium in the assays is derived from the fusion of acid-insoluble residues and functions as an enhancing agent. A similar SAA method carries the same design defect; 1.4 mg/ml sodium is used in the calibration standards and 1.15 mg/ml in the assays.[39] The sodium imbalance is derived from the use of sodium chloride in the calibration standards, whereas sodium carbonate is used as fusion agent for the assays. Apart from the imbalance of sodium cation concentration, a differing blank level for aluminum could be encountered. Fortunately, these defects have been recognized by ISO, and the sodium concentration is matched at 1.2 mg/ml in both calibration standards and assays and the sodium carbonate is blanked precisely.[48]

Fassel et al.[12] suggest that a selection of National Bureau of Standards (U.S.) Standard Reference Materials is ideally suited to prepare calibration solutions, and they recommend use for sequential determinations of a number of important elements in iron and steel by flame AES. Further, they suggest that if a congruent analytical calibration curve is obtained from a set of broadly based reference samples with no experimental points which depart significantly from the curve, the analyst may conclude that spectral, chemical, or physical interferences for the range of compositions studied either do not exist or do not make a significant contribution to the measured relative intensities.

The reviewer contests the view that the best function of a standard reference material is to provide the calibration standards when using solution techniques. It is considered better practice to prepare calibration series from pure reference materials for which certificated trace element analyses are available. It is also important to use matrix variations of major and minor elements to straddle the particular compositions of the samples being analyzed and to use random and statistically designed analyte calibration compositions to evaluate interference levels. Workers should make a thorough study of the potential interfering elements present within the band width of a selected analytical line and establish quantitatively the level of interference. The reviewer has seen numerous examples of the displacement of calibration standards because of an unrecognized general interference in calibration standard material because certain "tramp" elements settle at relatively consistent levels in steel-making practice (e.g., Cu, Ni, and Cr). This criticism does not extend to a statistically designed set of standards, such as National Bureau of Standards SRM 1261 to 1265, which contain certificated information on 40 elements together with iron in the range of 94 to 100 mass% and provide a useful basis for establishing potential interference levels within limited variations of iron composition.[70] Even so, many workers draw or calculate the calibration line of best fit for this set of standards without regard to interferences. Overall, the reviewer sees standard reference materials as ultimate arbiters in confirming that the developed procedure is satisfactory and that the interference coefficients developed from a series of calibration standards are correct.

In summary, it is essential that solution calibration standards match the assays in every way, including all pretreatments. There is a serious shortage of pure iron with a total impurity limit of < 1 μg/g with certified analyses for the impurities. It is recommended that the correct function of standard reference materials is to act as ultimate arbiter so that a developed solution procedure is satisfactory. Solid calibration standards should match assays with respect to structure and matrix.

IV. ANALYTE ATOMIZATION TECHNIQUES

A. General

The majority of published applications of AAS, AES, and AFS use a prepared solution for analyte atomization. Generally, direct nebulization of prepared solutions into a flame allows determinations in the range 0.001 to 30 mass%, covering a significant proportion of the total analysis requirements of the ferrous metallurgical industry. However, recent atomization techniques which have achieved significantly lowered limits of detection are hydride evolution and electrothermal furnaces. These recent techniques have engaged much attention because a means has been provided for obtaining many analyses which hitherto could not be easily achieved by existing techniques of analytical chemistry.

A number of techniques based on the direct sampling and analysis of solids have been proposed and supported by significant developmental research. However, there has been no upsurge in the use of these direct solid sampling techniques, and their fate may be determined by the newer goals to be established by development of the electrothermal furnace techniques.

Several types of atomic absorption spectrometers are commercially available. Simple attachments are available for the conversion of atomic absorption to atomic emission spectrometers. AES has enjoyed some resurgence due to improved instrumentation, utilization of the flames developed for AAS, and the development of inductively coupled plasma emission for multichannel spectrometry.[12] On the contrary, no commercial instrumentation is offered for AFS, confirming the relatively minor position occupied by the technique at the present time.[71] Improved support for AFS will not be forthcoming unless the technique is demonstrated to have distinct advantages over AAS for commercial samples.[72]

1. *Limits of Detection*

It is desirable to set out a comparative table of c_L values which may be achieved in ferrous materials by the various techniques of AAS, AES, and AFS and for the elements discussed in this review. The c_L values achieved with ferrous analyses are scattered throughout the literature and often not obtained with conditions giving optimum sensitivity. For AAS, Endo[3] has compared c_L values for analytes in relatively pure and 1% (mass/vol) iron media, concluding that a five-to-ten-times multiplier factor should be used for ferrous materials. The reviewer feels that a similar multiplier factor is appropriate for AFS. An additional difficulty with AFS is the use of higher temperature flames (to avoid massive interferences), resulting in poorer sensitivity. Accordingly, the various collections of published data for relatively pure solutions have been compared with selected results obtained with ferrous metallurgical solutions and factored to give estimated c_L values. With direct solids sampling and analysis, the position is less confusing, and the data are taken directly from the various papers.

An additional complication is caused by some workers defining the limit of detection as the concentration giving a signal of double the value of the standard deviation, whereas others use the concentration giving a signal equivalent to 1% A; still others use the concentration at which the signal-to-noise ratio is unity.

The reviewer feels that it is most convenient to convert the various c_L values to absolute concentration levels in the ferrous materials being analyzed. This basis permits a direct comparison of all solid and solution atomic spectrometric techniques, thereby aiding comparisons. Comprehensive tabulations are shown in Tables 2 and 3. The c_L values shown are based on conventional atomic spectrometric techniques and take no account of enhancement techniques such as solvent extraction or pulse nebulization.

The most striking features of the tabulations are the good c_L values achieved with the electrothermal GFAAS technique and the relatively small differences between elements; further significant improvements can be anticipated as instrumentation and know-how are improved.[76,77] While the GFAES mode is quite new, additional improvements can be anticipated.[4,47] The induction-heated GF vaporization of solids, when used in the AAS mode, achieves highly competitive c_L values, but further development may not be forthcoming due to the cost and lack of available standard reference materials.[8,61]

Hydride evolution in the AAS mode is applicable to a limited number of elements. However, in analyzing difficult trace elements in ferrous materials, the technique is more attractive than conventional nebulization. Significant improvements in c_L values will be achieved as analytical conditions are optimized and instrumentation refined.[58,78]

The c_L values achieved with conventional AAS, AES, and AFS nebulization have been optimized mainly by improved instrumentation; this is still the main avenue for further development.[71,73-75]

The cathodic-sputtering and glow-discharge techniques are not competitive on the basis of c_L values, and insufficient experimentation has been carried out to determine if the techniques are relatively interference free. It has been indicated that c_L values in the AAS mode could be improved by a tenfold increase in the absorption path. For the AES and AFS modes, improved c_L values are dependent upon improvements in apparatus design, and perhaps a longer term improvement of two- to threefold could be projected.[5-7]

2. *Improved Electrodeless Discharge Lamps*

While hollow cathode lamps (HCL) have tended to become the traditional source of radiation for AAS and AFS, significant advances have recently been made with programs to improve electrodeless discharge lamps (EDL). Higher brightness and stability of output have been achieved by[79-81] operation at 27 instead of 2450 MHz and passing heated air over the lamp envelope to control radiant output. Approximately 15 EDL sources are commercially available as recommended replacements for HCL. Specific advantages over the corresponding HCL are 5 to 100 times higher brightness, better stability, improved life for volatile element lamps, and better suitability for background correction techniques. For ferrous materials, the use of EDL achieved a twofold improvement in c_L values with conventional flame AAS, whereas for electrothermal furnace and

TABLE 2

Comparative Estimates of Limits of Detection (μg/g) of Analyte Elements in Ferrous Metallurgical Materials Using AAS Techniques

	AAS				
	Solid		Liquid		
Element	Cathodic[7] sputtering	Induction[8,61] furnace vaporization	Nebulized[73-75]	Electro-[76,77] thermal GF	Hydride[58,78] evolution
Ag			5	0.04	
Al		5	30	0.02	
As			40	0.3	0.5
Ba			50	0.1	
Bi		0.01	20	0.6	0.4
Ca			1	0.8	
Cd			1	0.01	
Co			5	0.1	
Cr	10		3	0.1	
Cu	10		2	0.1	
Fe			5	0.02	
Ga			70	0.6	
K			1	0.2	
La			2×10^3		
Li			0.6	1	
Mg			0.5	0.01	
Mn	60		2	0.02	
Mo	160		30	0.4	
Na			0.5	0.01	
Nb			1×10^3		
Ni	30		5	0.2	
Pb			10	0.1	10
Sb		0.8	20	0.3	0.6
Se			50	0.2	2
Si	400		100	0.2	
Sn		10	20	0.8	0.4
Te			50	0.4	2
Ti			90	1	
Tl			30	1	
V	90		20	1	
W			3×10^3		
Zn			2	0.004	

hydride evolution techniques, two- to fivefold improvements have been experienced.[79,80,82,83]

B. Direct Sampling and Analysis of Solids

Three significant sampling techniques which use solids directly for atomic spectrometric analysis may be classified as cathodic sputtering, aerosol generation, and furnace vaporization. Furnace vaporization from an induction-heated graphite well furnace has achieved the best c_L value (0.01 μg/g) recorded in atomic spectrometry.[8] The advantages of direct sampling and atomization of solids are that the reagents used for dissolution and laboratory wares are sources of contamination, dissolution causes considerable sample dilution and a corresponding poorer c_L, and solution preparation is a time-consuming step.[84]

1. Cathodic Sputtering

a. Apparatus

Grimm[5] described a glow-discharge sputtering tube suitable for direct atomic emission analysis of ferrous alloys; subsequent developments have led to simultaneous multielement analyses. Walsh[85] reviewed the methods of cathodic sputtering and

TABLE 3

Comparative Estimates of Limits of Detection (μg/g) of Analyte Elements in Ferrous Metallurgical Materials Using AES and AFS Techniques

AES			AFS		
Solid	Liquid		Solid	Liquid	
Glow[5] discharge	Nebulized[73]	Electro-[47] thermal GF	Cathodic[6] sputtering	Nebulized[71,73]	Element
	8	15		0.1	Ag
100	5	1		5	Al
	5×10^4			100	As
	2	4			Ba
	2×10^3			50	Bi
	0.1			1×10^{-3}	Ca
	8×10^2			1×10^{-2}	Cd
	30	10		5	Co
20	4	2	20	4	Cr
	10	3	20	1	Cu
	30	10		8	Fe
	10			10	Ga
	0.5	2×10^{-3}			K
	2×10^3				La
	0.5	0.1			Li
80	5	1		1	Mg
	5	4	70	2	Mn
10	100			60	Mo
	0.1	3×10^{-3}			Na
	60			1×10^3	Nb
	20	25	20	3	Ni
100	100			10	Pb
	600			50	Sb
	1×10^5			40	Se
5	5×10^3		400	600	Si
	300			50	Sn
	2×10^5			50	Te
	200			100	Ti
	20			8	Tl
	10			70	V
	5×10^2				W
	5×10^4			2×10^{-2}	Zn

described apparatus leading to further developments.[6,7]

The most recent cathodic-sputtering cell[7] that can be added to any standard atomic spectrometer in place of the conventional flame nebulizer provides a basis for discussing the formation of atomic vapor suitable for use with AAS, AES, or AFS. The cathodic-sputtering cell allows the solid sample to be made the cathode of a low-pressure inert gas discharge, whereby atoms are ejected from the sample surface by bombardment of energetic ions. Specifically, this cell eliminates many undesirable features of atomic vapors produced in flames, e.g., pressure broadening, quenching of fluorescent radiation, compound formation in flames, and opacity to vacuum ultraviolet radiation.[6]

A sputtering cell consisting of a borosilicate tube with quartz windows at either end is schematically shown in Figure 1. A flat surface on the top side contains an O-ring which seals the specimen to a silica annulus on the cell and enables rapid interchange; an anode, pumping port, and gas inlet tube are provided.

A schematic diagram of the replaceable silica annulus is shown in Figure 2, and the four main

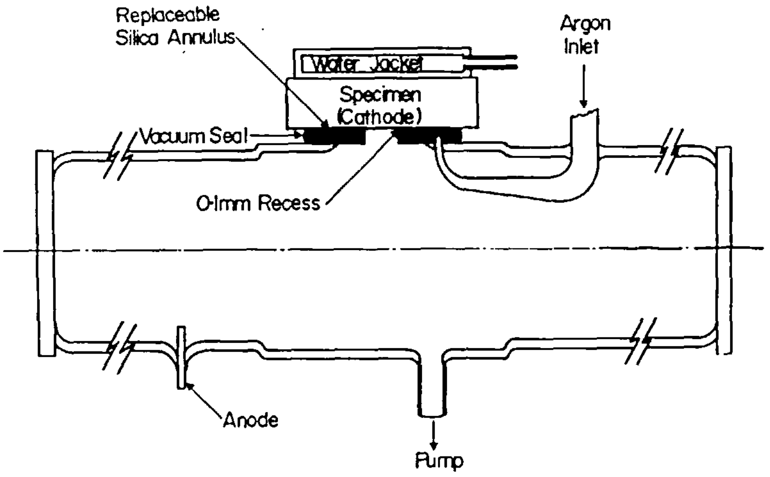


FIGURE 1. Schematic diagram showing sputtering chamber and mounted specimen. (Reprinted with permission from Gough, D. S., *Anal. Chem.*, 48, 1926 (1976). Copyright by the American Chemical Society.)

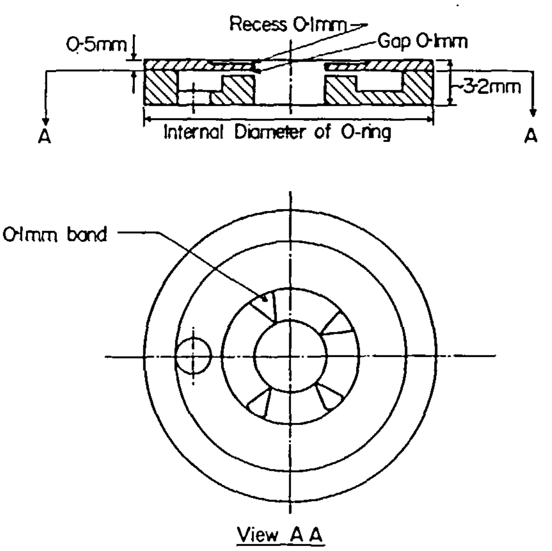


FIGURE 2. Schematic diagram showing hollow silica annulus and gas ports. Diagram is not to scale as the gap and recess dimensions have been enlarged for clarity. (Reprinted with permission from Gough, D. S., *Anal. Chem.*, 48, 1926 (1976). Copyright by the American Chemical Society.)

features, which are designed specifically for AAS but generally applicable, are

1. The small recess in the top surface confining the discharge to the center hole is too small to allow sputtered vapor to diffuse between the top surface of the annulus and the cathode; thus, the cathode remains electrically isolated.

2. The flow of pure argon gas at the specimen surface sweeps away gaseous impurities, thus, reducing reaction with readily oxidized elements such as aluminum.

3. The gap in the hollow annulus admits gas into the chamber at high speed; accordingly, few atoms diffuse into this gap.

4. The gas flow past the specimen which prevents some diffusion to the cathode or nearby sinks, and the sputtered atoms are swept into the chamber at 900 cm/sec, which is much greater than the normal diffusion speed of metal vapor in argon gas.

The advantages of the technique are the ability to remove thin layers from a surface in a well-controlled manner and limited matrix interference effects from varying metallurgical phases. The disadvantages include the necessity to present a flat smooth frontal surface of not less than a 30-mm diameter to achieve adequate sealing and a flat back surface to ensure effective water cooling in order to prevent thermal vaporization, outgassing, oxidation, and self-diffusion within the specimen.[7] The minimum sample diameter is a severe disability for many commercial specimens.

b. General Application

i. Atomic Absorption Spectrometry

Trace elements give small absorbance readings with the cathodic-sputtering cell of Gough;[7] however, background noise is very low. Accordingly, the output signal is amplified to make accurate measurements even though significant drifts in light source intensity and background absorption occur. A dual-modulation amplifier was developed to automatically compensate for these drift variations; thus, the HCL is modulated at a predetermined frequency (320 Hz) while the sputtering discharge is modulated at a submultiple (10 Hz); the resulting signal is amplified and separated into two components.

Although sputtering is free from certain background effects which can occur in a flame, background nonatomic absorption can occur and is typically 0.25 to 2%. The recommended grating monochromator has a dispersion of 3.3 nm/mm and is similar to units commonly used for AAS. A two-stage rotary backing pump was used to maintain a 0.3 l/min argon gas flow at a constant pressure of 0.6 kPa. The most suitable sputtering power (50 mA at 800 V) for iron alloys achieved a sample removal rate of 400 μg/min. Stabilization of voltage and current was not mentioned, but this would be desirable. Dry argon gas containing maximum impurity levels of 6 μl/l O_2, 1 μl/l H_2, 5 μl/l CO_2, 20 μl/l N_2, and 20 μl/l H_2O was used. With the exception of water vapor, the effect of these impurities on the sputtering efficiency is insignificant; accordingly, the only gas purification column required was a molecular sieve trap.[7]

The specimen analysis time required for each analyte is 3 to 5 min: 20 sec to adjust the gas in the chamber to the requisite pressure, 1 to 2 min to obtain a steady signal, and 1-min integration time. The spectrometer was calibrated using British Chemical Standards, low-alloy steel standards; however, the actual catalog numbers were not disclosed. A series of ten readings was taken for each element, and the sample was removed, resurfaced, and replaced after each individual reading in order to present a fresh surface. Calibration curves passing through the origin were obtained for each analyte, indicating that satisfactory background correction was being achieved. The relevant precision and detection limit data obtained by Gough[7] with an absorption path length of 1 to 2 cm are shown in Table 4. It is suggested that the path length could be increased to 10 to 20 cm with a corresponding c_L improvement. A better estimate of the capability of the technique would have been available if a set of "unknown" samples of differing metallurgical history had been compared with the calibration curve.

TABLE 4

AAS Data Achieved for Cathodically Sputtered Iron Alloys

Concentration, element	λ (nm)	S_r (%)[a,b]	c_L[c,d] (μg/g)
3.1%, Ni	232.0	0.7	30
1.2%, Cr	357.9	0.9	10
1.0%, Si	251.6	2.2	400

[a] Relative standard deviation percent.[13]
[b] n = 10.
[c] Basis of calculation for c_L not disclosed.
[d] Absorption path length, 1 to 2 cm.

A significant advantage of cathode sputtering AAS is the ability to analyze surfaces and hence measure composition as a function of depth. Some of the perceived limitations at this stage of development are the requirement for a sample with a relatively large diameter ($\approx$ 30 mm), a relatively slow speed of analysis ($\approx$ 4 min) (which is not competitive with the alternative techniques of OES and XRFS), the need for samples and calibration standards with a similar metallurgical history and alloy grouping, and poor precision with analytes which scavenge oxygen (cf., silicon, Table 4).

Future studies could be aimed at the following matters: determining whether the poor precision achieved with oxygen-scavenging elements such as silicon can be overcome by improved gas quality and cell design, designing and testing an internal standard second channel to compensate for sputtering differences between samples, and modifying the instrumental design to allow the determination of elements such as sulfur and phosphorus for which the useful absorption lines occur below 190 nm.

ii. Atomic Emission Spectrometry

Significant applications of the glow-discharge tube have been achieved for multielement direct reading OES.[5] However, the original development was achieved in a dual-channel mode, and the specific discharge conditions found most suitable for a 50 mass% Ni-Fe binary alloy were a pressure of 1.4 kPa (± 0.01) and a current of 200 mA (± 0.1). The analysis time per specimen was 2 min, composed of a warm-up time of 90 sec to reach equilibrium and of 20- to 40-sec integration times; however, it was suggested that a warm-up time of 30 sec would be adequate for routine analyses.[5]

Variations in matrix metallurgical conditions and sputtering rate were overcome by using either nickel (361.0 nm) or iron (302.0 nm) line as internal standard elements for a 50% Ni-Fe binary alloy. A satisfactory calibration curve was obtained for 0 to 150 μg/g silicon using 288.1 nm with nickel (361.0 nm) as internal standard. The elements and wavelengths (nm) examined and the c_L (μg/g) achieved were, respectively, Al–396.2, 100; Cr–425.4, 20; Mg–279.6, 80; Mo–386.4, 10; Pb–405.8, 100; and Si–288.1, 5. The relative standard deviations achieved for most elements were 0.6%.[5]

Future studies could make progress by establishing the effect of metallurgical history and differing alloy groups on precision and accuracy, using modern electronic equipment to monitor background and sputtering rate to compensate for emission differences between samples, developing the technique for a dedicated quality control function, examining application to the determination of elements such as sulfur and phosphorus at wavelengths below 190 nm (as development could be achieved more readily than with the AAS mode), developing application for refractory elements such as silicon and niobium which give notoriously poorer sensitivities in the AAS mode,[7] and reducing the minimum sample diameter which can be analyzed.

iii. Atomic Fluorescence Spectrometry

The original atomic fluorescence sputtering cell[6] has been superseded by an improved version described for AAS.[7] The experimental optical and electronic arrangements used for detecting atomic fluorescence are shown schematically in Figure 3. Modulated radiation from an intense light source of an appropriate element illuminates the sputtered vapor, and the atomic fluorescence is detected at right angles to the incident light beam with a photomultiplier tube. The modulated fluorescence signal is separated from DC emission in the sputtering chamber by synchronous demodulation.

The lamp sources were filled with neon to eliminate the possibility of detecting fluorescence contributions from metastable argon atoms present in the sputtering discharge. Light losses are reduced and simplicity is achieved by not using a monochromator. Accordingly, the fluorescence radiation is detected with a "solar blind" photomultiplier tube (Hamamatsu R166) in the deeper UV region (Fe, Ni, Mn, and Si) or a S19 response photomultiplier tube (Hamamatsu R106) plus interference filter for the near UV and visible region (Cr and Cu). A two-stage rotary vacuum pump was used to maintain a 0.2 l/min argon gas flow at a constant pressure of 0.6 kPa, and the gas purity is described in Section IV.B.1.b.i. The most suitable sputtering conditions for iron alloys were 35 mA at 300 V. The analysis time per specimen was 4 min since 1 to 2 min was necessary to achieve sputtering equilibrium.[6]

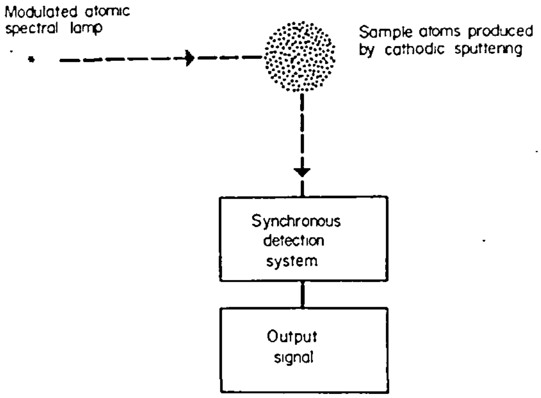


FIGURE 3. Schematic diagram showing the experimental optical and electronic arrangement for measuring atomic fluorescence from cathodically sputtering atomic vapor. (Reprinted from Gough, D. S., Hannaford, P., and Walsh, A., *Spectrochim. Acta Part B*, 28, 197 (1973). With permission.)

A series of readings was taken using British Chemical Society low-alloy steel standard reference materials SS401 to 410 (inclusive) and a relative standard deviation of 1% was achieved at 1.69% nickel. c_L values of 20 μg/g were achieved for Ni, Cr, and Cu; 70 μg/g for Mn; and 400 μg/g for Si. The calibration curves did not pass through the origin, particularly for Si, Cr, and Mn; this was thought due to additional fluorescence from elemental impurities, probably iron in the cathodes of the source lamps. This particular difficulty could be considerably reduced by using a monochromator.[6]

The advantages of the AFS technique over AAS are that relatively high sensitivities can be obtained at low sputtering currents when high intensity lamps are used and the fluorescent radiation can be readily isolated without the requirement of a monochromator. The AFS technique has been favorably contrasted with AES: the signal intensity depends on the concentration of ground state rather than excited state atoms, and the occurrence of spectral interference is significantly reduced.[6]

The observed advantages and limitations of the technique are relatively similar to those described for AAS cathodic sputtering as discussed in Section IV.B.1.b.i. Future studies of the style discussed in Sections IV.B.1.b.i and IV.B.1.b.ii would give an increased understanding of the future value of the technique.

2. *Aerosol Generation*

a. Apparatus

An apparatus proposed by Winge et al.[84] used aerosol generation and transportation of metallic particles to a relatively conventional N_2O-C_2H_2 burner, which can be inserted into a standard flame atomic spectrometer. A schematic diagram of the aerosol generator is shown in Figure 4. The generator consists of a small assembly, sealing against the flat surface of a sample. The flat surface need be only 40 mm in diameter, although samples as small as 13 mm can be used. A 3.25-A, DC arc discharge (250 V open circuit, spark ignited) takes place between the cathodic sample and the end of a small copper tube (which serves as anode), and an argon gas flow of 6.3 l/min gives maximal atomization efficiency without affecting flame stability. Boron nitride fabrications are used for insulation and to confine the discharge to the end of the tube anode. The arc discharge causes cathodic ejection of small droplets of molten metal, which are converted to an aerosol of metallic particles. The sputtering rate is proportional to the square of the arc current, and the aerosol production rate is a function of arc current and gas composition. With 3.25 A, the sputtered mass corresponds to 3 mg/min. An inlet adapter replaces the conventional nebulizer in the burner-flame assembly, and a flow spoiler is not used. The analysis time per specimen was 25 sec, with a 15-sec prearc period to stabilize the discharge and an 8-sec integration period.

Relatively similar aerosol generators have been subsequently described for ferrous alloys, and particular emphasis has been given to the remote-sampling capability. Transfer distances of up to 20 m between aerosol generator and monochromator excitation source have successfully been used.[86-88]

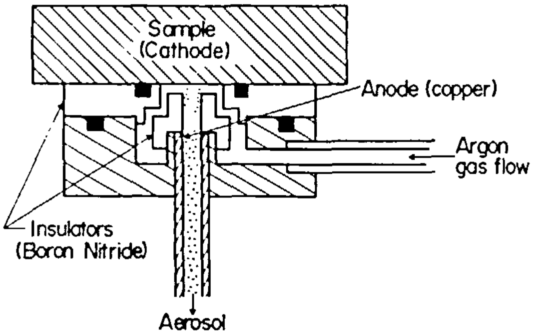


FIGURE 4. Schematic diagram of an aerosol DC arc generator. (Reprinted from Winge, R. K., Fassel, V. A., and Kniseley, R. N., *Appl. Spectrosc.*, 25, 636 (1971). With permission.)

b. General Application

Winge et al.[84] describe applications for AES and AAS, and, undoubtedly, the aerosol is suitable for the AFS technique. Flame AES has been applied under laboratory conditions to the determination of 0.01 to 1% chromium in low-alloy steel, where a relative standard deviation of 2% was achieved for four locations on a single sample.[84] Linde and Sitek[87,88] designed a flame AES, portable manganese analyzer for separating mixed steel. A relative standard deviation of 5% was achieved for 0.3 to 2% manganese.

Application to flame AAS was illustrated by the determination of 0.02 to 2% manganese in steel, while some initial difficulty was experienced with a radiofrequency (RF) interference (from arc excitation chamber); this was overcome by using an 8-m length of Dekoran® tubing between the generator and spectrometer. Deviations as great as 10% (relative) from the calibration curve were experienced.[84]

The limitations of the aerosol technique appear to be that the precision data are not competitive with solution-nebulization techniques for similar analyte concentration ranges and that the detection limits are not competitive with cathodic sputtering. The advantage of the aerosol technique, compared with all other techniques discussed in this review, is that sampling may be achieved at remote locations from the spectrometer without affecting signal response or experiencing a memory effect.

Suggested developments include the use of a double-channel system to incorporate the internal standard technique in an endeavor to achieve improved precision, the use of a secondary arc discharge rather than a flame in the AES mode (this arrangement would also allow the analysis of sulfur or phosphorus at wavelengths below 190 nm),[86] and establishing the effect of metallurgical history and differing alloy groups on precision and accuracy.

3. Furnace Vaporization

a. Apparatus

The apparatus developed by Headridge and Smith[9] uses an induction-heated graphite furnace coupled to a conventional atomic spectrometer. A schematic diagram of the furnace is shown in Figure 5. The carbon core is centrally bored to within 10 mm of one end. The light guides are 75 mm long, 15 mm O.D., and 6 mm I.D., and positioned on either side of the core (which is shrouded with a quartz tube); the between space (E) is packed with -40-μm insulating graphite. The core is heated with a six-turn induction coil wound around the quartz sheathing, and the RF power is supplied by a 6-kW induction generator. The entire assembly is enclosed in an asbestos box containing inlet and outlet argon gas tubes and two fused silica windows in line with the light guides. Samples are introduced through a double valve, which prevents air ingress, and a graphite funnel is positioned directly above the bore of the graphite core to guide solid samples into the hot furnace. Metal samples of 4 to 10 mg may be dropped into the furnace where atomic vapor is formed from volatile components and passes through the absorption path provided by the light guides and silica windows.

b. General Application

Headridge and Smith[9] reported a calibration curve for 0.3 to 100 μg/g bismuth in steel, and subsequently Hunter et al.[8] achieved a c_L of 0.01 μg/g for the same determination. Ashy et al.[61] reported further results, although the lack of suitable standard reference materials prevented adequate validation of the technique. A compilation of the data achieved by the various authors is summarized in Table 5.[8,9,61]

A seemingly more important sample presentation technique was that of microdispensing small

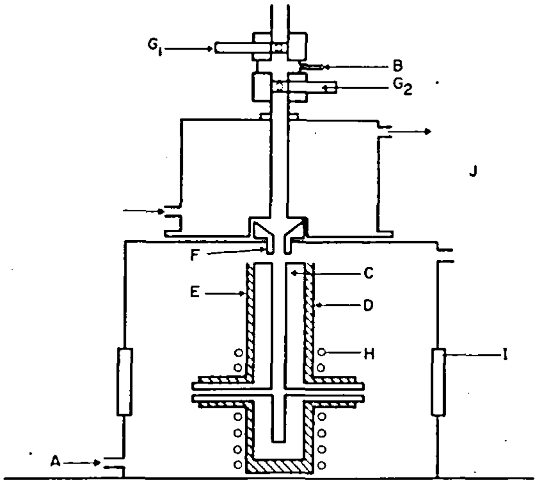


FIGURE 5. Schematic diagram of an induction-heated graphite furnace for atomic spectrometry. (A and B) Argon inlet; (C) graphite core; (D) quartz sheath; (E) graphite insulation; (F) graphite funnel; (G_1 and G_2) Econ-O-Miser® ball valves type 44/46/T (Worcester Valve Co. Ltd.) of 13-mm nominal bore; (H) induction coil; (I) fused silica windows; (J) aluminum cooling jacket for cold-water circulation. (Reprinted from Headridge, J. B. and Smith, D. R., *Talanta*, 19, 833 (1972). With permission.)

TABLE 5

AAS Data Achieved with Solid Samples in an Induction-heated Graphite Furnace[8,9,61]

Element	λ (nm)	Temperature (°C)	Calibration range (μg/g)	c_L (μg/g)	S_r (%)	Concentration (μg/g)
Sn	284.0, 286.0	2400	140–850	10	9	320
Sb	231.1	2400	20–260	0.8	7	170
Al	309.3	2450	130–930	5	7	460
Bi	206.8[a]	2400	5–100	0.3	8	65

[a] The reviewer presumes that Ashy et al.[61] used 206.2 nm.

volumes of nitric acid media solutions onto carbon pellets (6 mm diameter X 3 mm high).[9] After evaporation of solvent to produce a solid deposit, the carbon pellets were added to the induction-heated furnace in a manner similar to solid standard reference materials. A calibration curve was presented, but the obvious advantage of the method for overcoming the lack of suitable solid standard reference materials was not discussed.

The limitations of the technique are as follows. The concentration range (which can be analyzed) is limited by stringent restrictions on sample weights (4 to 10 mg). The method is absolutely dependent on the availability of standard reference materials with the appropriate concentration range for each matrix and analyte, which is a very severe limitation at the present time for 0.01 to 10 μg/g of analytes (Section III.C). The technique is tedious and slow, and the rise time of approximately 160 sec for the production of atomic vapor is a limitation for the chosen example of high boiling aluminum in steel; accordingly, peak area rather than peak height is the relative measurement parameter. The slow rise time limits the dynamic concentration range (which can be analyzed); the induction-furnace assembly used was limited to a maximum temperature of 2450°C, although it was predicted that a temperature capability of 3000°C would be required to exceed the boiling point of the iron matrix, which, in turn, would decrease the rise time and improve the sensitivities. The advantages of the technique are the avoidance of contamination problems associated with sample dissolution and certain obvious injection and aerial contamination problems associated with electrothermal furnace techniques.

Suggested developments include a full evaluation of the technique of evaporating solutions on a carbon pellet for addition to the furnace (avoiding the lack of standard reference materials) and the evaluation of the technique for AFS where lowered c_L values with minimum interference may be achieved.

C. Analysis of Liquids

The majority of analyses using atomic spectrometry are based on solutions. The major factors to be overcome during the analysis of iron matrix solutions are preparation difficulties in dissolving the sample, production of atoms of analytes, and matrix effects.[89] Further, simultaneous minor and major alloying element determinations with the one-solution preparation impose, respectively, simultaneous requirements for high sensitivity and accuracy to be achieved.[3] Metallurgical solutions are characterized by the presence of the major matrix element iron, major alloying elements, and significant concentrations of anion(s) introduced by the dissolution process. A 1% (mass/vol) iron (III) dissolution in perchloric acid media is equivalent to 7% (mass/vol) ferric perchlorate solution in excess perchlorate anion.[65] Generally, minor concentrations of iron interfere with an analyte; however, iron, as a major matrix element, is usually successful in suppressing interferences from other alloying elements and achieving a plateau effect for varying but major iron concentrations.[3,58]

The significant solution techniques of atomic spectrometry discussed in the ensuing sections are nebulization, hydride evolution, and electrothermal atomization. The published applications of AES and AFS in these categories are minor when compared with AAS; accordingly, the review of solution methods is grouped under the various analyte atomization techniques.

1. Nebulization

a. Apparatus

The design of atomic spectrometers is primarily aligned with the requirements of techniques based on continuous solution nebulization. Furthermore, the premix laminar flow burner has assumed the dominant role for nebulization and atomization in AAS and AES.

The unique development of repetitive optical scanning devices has proven effective for AES and could be incorporated in commercial atomic spectrometers. These devices, together with associated electronics, enable corrections for unwanted backgrounds and/or overlapping bands resulting from matrix or flame components and allow significantly improved c_L and S_r values.[22,90] Repetitive optical scanning devices could also be used for simultaneous nearby line or continuum-light background correction techniques, which are assuming a more important role in AAS[91] (Section IV.C.1.d.iii). Alternatively, the more costly double-monochromator systems should be used.

Fernandez and Kerber[11] discuss a recent commercial instrument, which has all functions controlled by a microprocessor-based minicomputer. Assessments are required to determine the degree of confidence with which this generation of instruments can be applied to the analysis of major alloying elements, particularly 5 to 50 mass%. The precision achieved with AAS has been compared with integration time, as shown in Figure 6, using four elements and two flames in order to give a good representative overview of performance expectations. Precision improved as a function of square root of integration time to settle at relatively stable relative standard deviations of 0.12% to 0.22% after an integration time of 10 sec.

Precision as a function of absorbance at a fixed integration time of 10 sec is shown in Figure 7, where four elements and two flames are used. Precision values obtained from replicate AAS determinations are plotted against the absorbance of the various calibration standards. For the elements studied, relative standard deviations range from 0.18 to 0.24% for the absorbance range 0.1 to 1.[11]

Optimum precision over this wide absorbance range permits the analysis of major alloying elements with minimal dilution, and the microprocessor electronics permit automatic calibration between closely bracketed standards. For example, a 0.1% (mass/vol) solution of 18/8 stainless steel (NBS, SRM 101e) was prepared in 1.5% (v/v) HCl + 0.5% (v/v) HNO_3 media. Ten samples were prepared, and nickel absorbance was read ten times for each sample solution, using 10-sec integration and bracketing between 8.41% Ni (A = 0.618) and 10.51% Ni (A = 0.702). The ten mean results for nickel fell within the range 9.48% (± 0.05%), and the relative standard deviation of 0.4% was primarily determined by instrumental factors. Similarly, for chromium and manganese, the results were 18.64% (± 0.04%, relative standard deviation = 0.15%) and 1.78% (± 0.008%, relative standard deviation = 0.27%), respectively.[11] These results can be compared with the achievements of earlier workers. Gregorczyk[92] prepared a 0.1% (mass/vol) solution of stainless steel in 0.75% (v/v) H_3PO_4 + 0.75% (v/v) H_2SO_4, and, following fuming, matrix-matching, and bracketing of calibration standards, relative standard deviations of 0.6, 0.5, and 0.6% were obtained at 11% Ni, 20% Cr, and 13% Mn, respectively. Thomerson and Price[10] prepared a 1% (mass/vol) solution of stainless steel in 10% (v/v) $HClO_4$, and, using a differential reading technique for chromium (150 to 250 mg/l), they obtained a relative standard deviation of 1% at 25% Cr level.

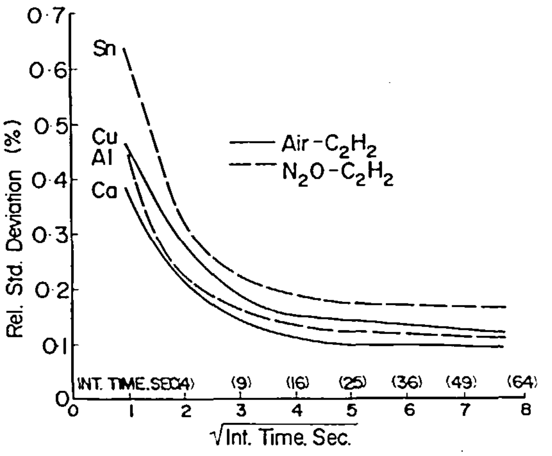


FIGURE 6. Precision as a function of integration time measured for Ca and Cu (air-C_2H_2) and Al and Sn (N_2O-C_2H_2) using a microprocessor atomic absorption spectrometer. (Reprinted from Fernandez, F. J. and Kerber, J. D., *Am. Lab.*, 8, 49 (1976). With permission.)

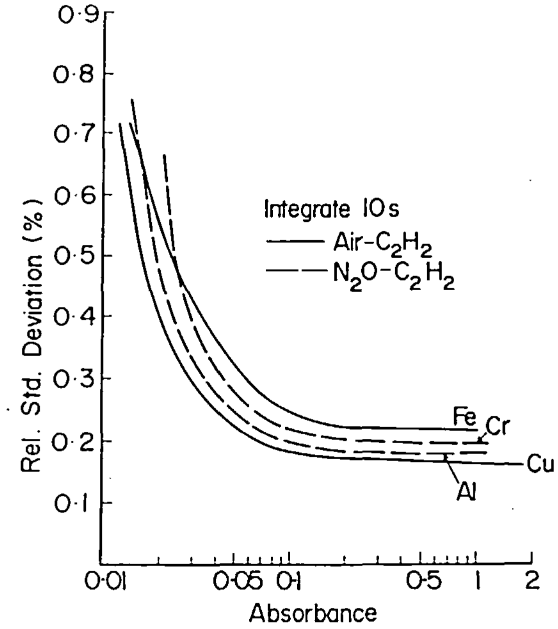


FIGURE 7. Precision as a function of absorbance for Cu and Fe (air-C_2H_2), and Al and Cr (N_2O-C_2H_2), with 10-sec integration using a microprocessor atomic absorption spectrometer. (Reprinted from Fernandez, F. J. and Kerber, J. D., *Am. Lab.*, 8, 49 (1976). With permission.)

Accordingly, for recent atomic spectrometers based on microprocessor control, it can be concluded that: the precision and accuracy values obtained are consistent with the requirements of good commercial analyses for major alloys in ferrous materials; further replacement of existing classical techniques by atomic spectrometric techniques will be achieved; the bracketing of and the precise matrix-matching of the calibration will achieve maximum precision and accuracy; the improved precision will benefit the entire concentration range of analyte elements; and the improvements will be applicable generally to AES and AFS.

b. Pulse Nebulization Technique

Workers determining minor concentrations of analytes may encounter a sample solution concentration barrier beyond which rapid burner blockage is experienced, if the traditional method of continuous nebulization is used. The iron concentrations of 2 and 1% (mass/vol) for premix laminar flow burners using air/C_2H_2 or N_2O/C_2H_2, respectively, or 0.5% (m/v) for a total consumption burner should not normally be exceeded.[53,93-95]

Apart from burner blockage, increasing iron concentration beyond the suggested levels actually reduces the ground-state atomization efficiency of the analyte in AAS. Furthermore, the background absorption due to increasing iron concentration continues to increase, particularly when using air-C_2H_2 in the range 200 to 300 nm. Thus, sensitivity actually declines even though an increasing concentration of analyte is supplied to the nebulizer. These phenomena, illustrated in Figure 8, were actually experienced by Sauer and Nitsche[96] when developing conditions for the determination of gallium in steel using continuous nebulization. Accordingly, a pulse nebulization technique, using discrete sample nebulization aliquots of 25 to 200 μl, has been recommended and developed, and a suitable sampling cup is commercially available.[8,53,97-100] The primary advantage of this technique is the opportunity to obtain satisfactory results without resorting to separations because c_L values can be improved sevenfold.[53]

Ambrose[98] developed pulse nebulization for the direct AAS determination of aluminum in steel, and, with 150- to 200-μl aliquots of 4% (mass/vol) iron solutions could be used without burner blockage. A standard N_2O-C_2H_2 flame with a 0.4-mm slot burner was used, and the achieved c_L of 7 μg/g was sufficient to avoid the alternative of carrying out a preliminary separation. Furthermore, a significant improvement in precision was achieved by the use of pulse (relative standard deviation = 1.6%) as compared with continuous nebulization (relative standard deviation = 6.4%) at the 250 μg/g level. A study of the variation between peak height and injected aliquot supported the use of a minimum volume of 150-μl aliquots.

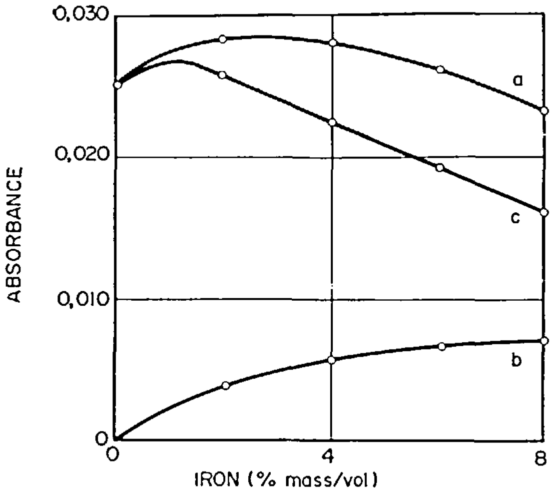


FIGURE 8. Influence of iron concentration on the absorbance of gallium when using 294.4 nm and air-C_2H_2. (a) Iron matrix + 15 μg/ml gallium; (b) iron matrix + 0 μg/ml gallium (iron background); (c) iron matrix + 15 μg/ml gallium (corrected for iron background). (Reprinted from Sauer, K. and Nitsche, M., *Arch. Eisenhuettenwes.*, 47, 153 (1976). With permission.)

Recently, Thompson and Godden[53] developed a wider slot (0.6 mm) burner head, which uses a support gas of 15% N_2/85% N_2O and can be used with 10% (mass/vol) iron solutions; 200-μl aliquots were found to give the best compromise with respect to signal-noise ratio and the absence of blockage in the burner slot. The pulse technique was applied to the AAS determination in steel of aluminum, arsenic, and tin.

However, pulse nebulization is no instant panacea to improve the c_L value for all elements. Thus, Ambrose[98] studied the AAS determination of antimony, bismuth, and lead in steel using up to 4% (mass/vol) iron media, but found that significant and excessively variable backgrounds affected S_r and c_L; air-C_2H_2 flame was used, and significant background absorbances were experienced at 200 to 300 nm, even with 1% (mass/vol) solutions.

Thompson and Godden[53] experienced several difficulties when applying background correction methods because the increased iron concentration embodied in the 10% (mass/vol) solutions amplified many background and spectral interferences which are normally benign. Thus, if c_L is improved sevenfold and the iron concentration is increased tenfold, then an amplification factor of 70 for background and spectral effects could be experienced. Provided proper consideration is given to the various contributing factors, a selection of the various background correction techniques (Sections IV.C.1.d.ii to iv) should be successful for each specific determination, and further studies are warranted.

Another matter requiring evaluation is a consideration of the acid volumes actually required to dissolve the larger sample masses. The reviewer feels that excess acid concentration should be limited in order to avoid the twin problems of burner system corrosion and concomitant introduction of analytes. It is interesting to note that Thompson and Godden[53] used 10% (mass/vol) iron in 37% (v/v) HCl + 13% (v/v) HNO_3 and Ambrose[98] used 4% (mass/vol) iron in 40% (v/v) HCl, whereas Hunter et al.[8] used 6% (mass/vol) iron in 10% (v/v) HNO_3. Perhaps, there is a compromise on the rate of sample solution, but the reviewer supports the need for a study to reduce the acid concentration proposed for pulse nebulization, and, apart from reduced corrosion effects, solution viscosities and anion concentrations would be beneficially decreased.

The c_L values achieved with AAS pulse nebulization are not competitive with electrothermal atomization and hydride evolution;[8] nevertheless, the convenience, relatively low cost, and the potential to avoid preliminary separations suggest that further development is justified. Due to massive interference problems, the pulse nebulization technique would not appear to be applicable to AES and AFS.

c. Flames

Certain difficulties with AAS burners and flames affecting the ability to obtain concordant results between differing laboratories are discussed in Section III.A.

Fassel et al.[12] have discussed three essential features of the burners and flames required for flame AES: a nebulizer-spray chamber burner for premixing of oxidant, fuel, and aerosol; a chemical environment conducive to efficient atomization; and a sufficiently high temperature to provide optimal signal to noise ratios. The authors concluded that these essential features are conveniently provided by commercially available N_2O-C_2H_2 slot burners designed especially for flame AAS.

Ottaway[19] indicates that although flame AFS sensitivities are best in hydrogen flames which limit quenching, higher temperature flames are required for ferrous solutions because serious chemical interferences are experienced with lower temperature flames. This general observation was confirmed by Michel et al.[101] who determined tin in steel using an air-C_2H_2 flame.

Sundberg[46] carried out an extensive study of flame characteristics and AAS sensitivity and issued a stern warning that operators should not adjust to best sensitivity conditions with matrix free solutions and then assume suitability for complex solutions generated from commercial alloys. It was concluded that for any given gas flow ratio, the flame is not uniform over any vertical dimension because of the existence of marked differences in shape, composition, and temperature. Accordingly, for the sensitive complex equilibria that occur in the flame, there should be a discrete zone that contains the greatest population of free atoms per unit volume for each differing matrix. Sundberg[46] warns that if standards are not matched to samples with respect to bulk matrix, then the respective optimum zones for maximal production of free atoms may not coincide and, accordingly, the inevitable sensitivity losses, deviations from the standard calibration curve, interferences, and differences between laboratories are encountered.

Rubeska[102] has discussed analyte reduction in fuel-rich flames as a source of interference with flame AAS and has suggested that the adverse effects of strongly reducing media on the vaporization of the analyte (through formation of involatile metal or carbide) were left unnoticed for a long time and that the almost unspecific enhancement of molybdenum by refractory oxides occurs by hindering the reduction of molybdenum oxides before vaporization either simply by shielding from reducing gas or by reactions taking place in the condensed phase at higher temperatures. Accordingly, slight changes in experimental conditions in fuel-rich flames have a major influence on observed interferences, and disagreements between different authors are common.

Several AAS investigators have chosen the N_2O-C_2H_2 flame so as to avoid many difficulties with air-C_2H_2; the protagonists of air-C_2H_2 usually point to the poorer c_L experienced with N_2O-C_2H_2. Fleming[103] studied chemical and spectral interferences with the AAS determination of cobalt in steel using the 240.7-nm line and an air-C_2H_2 flame. The unsatisfactory nature of earlier investigations was disclosed by the SAA through comprehensive studies of high- and low-alloy steels. Accordingly, 1% (mass/vol) solutions in three common acid media of 10% (v/v) HCl, 10% (v/v) $HClO_4$, and 3% (v/v) H_2SO_4 + 3% (v/v) H_3PO_4 were studied using oxidizing and reducing, air-C_2H_2 flames, and a fixed observation height. The results showed variable background absorbance by iron and nickel and serious variations in absorbance unless a highly oxidizing flame was used to give less than maximal cobalt sensitivity. Even though c_L was poorer by a factor of 2.5, Fleming[103] recommended the use of N_2O-C_2H_2 and 10% (v/v) perchloric acid media since matrix effects (due to alloying elements) and background absorption (due to iron) did not occur.

Cobb et al.[104] disagreed with Fleming[103] when studies using oxidizing air-C_2H_2 optimized to maximal absorbance with a solution containing iron and cobalt were carried out with 2% (mass/vol) iron in 20% (v/v) HCl + 2% (v/v) HNO_3. No interferences were experienced from typical elemental concentrations in steel whether examined individually or blended for the ranges 70 to 100% Fe, 25% Cr, 20% Ni, 12.5% Mn, 5% Cu, 2.5% Mo, 2% V, and 2% Ti. However, there appear to be several problems with the study,[104] e.g., the potential interference of silicon was not evaluated, only one cobalt concentration of 0.03% for the limited range 0 to 0.05% was studied, the calibration curve did not pass through the origin, and the implied level of background is consistent with the alternative viewpoints.[103,105]

The ASTM method[35] for magnesium in iron ore by AAS suggests that a threefold loss of sensitivity is experienced if N_2O-C_2H_2 is used; hence, they propose air-C_2H_2 together with a lanthanum addition to overcome suppression effects. However, the relatively similar SAA method[40] uses N_2O-C_2H_2 together with a lanthanum addition in order to achieve an enhancement plateau effect. Notwithstanding, the reviewer notes that the recommended calibration concentration ranges are relatively similar, being 0.5 to 2.5[35] and 0.2 to 3 μg/ml.[40] Again, the SAA method[41] for manganese in iron ore chooses the somewhat poorer sensitivity of the N_2O-C_2H_2 flame rather than the conventional air-C_2H_2 flame specifically to avoid interference due to variable concentrations of calcium, aluminum, and iron.

Husler[106] recommended N_2O-C_2H_2 for the AAS determination of Cr, Mn, Mo, V, and W in tool and high-alloy steels to minimize chemical interferences. Scholes[44] edited a collaborative study of chromium in iron and steel by nine laboratories (using seven differing models of atomic absorption spectrometers) and noted the almost total lack of interferences in N_2O-C_2H_2 as compared with air-C_2H_2. Thomerson and Price[10,67] reported that when 1% (mass/vol) iron in 10% (v/v) $HClO_4$ media (analytes, Al, Cr, Sn, Ti, and V), or 10% (v/v) $HClO_4$ + 10% (v/v) H_2SO_4 + 10% (v/v) H_3PO_4 media (analytes, Mo and W) are used for AAS determinations with N_2O-C_2H_2, interference-free methods for low- and high-alloy steels are achieved.

Future studies should attempt to resolve the suitability of the two flames, air-C_2H_2 and N_2O-C_2H_2, with respect to certain elements discussed in this section. The reviewer feels that N_2O-C_2H_2 flames have shown some obvious advantages and that there is merit in developing cooler N_2-N_2O-C_2H_2 flames for readily ionized analytes. These studies would resolve a variety of conflicting data advised by differing laboratories, and it should be possible to locate a flame temperature and stoichiometry appropriate to each concentration of iron matrix for each analyte. The choice of an optimal flame should minimize background interferences and give the best detection limits consistent with minimal interferences and suppression (Section IV.C.1.d).

d. Interferences and Corrective Techniques

i. Spectral Interference and Corrective Techniques

Lovett[107] used three classifications to describe spectral interferences in AAS: observed direct spectral overlaps, neon emission lines, and predicted spectral overlaps. However, the literature carries only a limited number of references to the occurrence of these interferences in ferrous metallurgical analyses.

Two specific modes of spectral interference should be recognized in AAS.[3,23,53,91,96]

1. A nonanalyte element (a), which is present in a matrix and has a nearby absorption line to the analyte absorption line, can absorb the analyte lamp signal in proportion to the concentration of element (a) in the matrix; thus, iron (213.859 nm) interferes when zinc (213.856 nm) is being determined in ferrous materials, even if iron is totally absent (nonsignificant) in the zinc source lamp.

2. The impurities in the element used for the source can, if included in the spectrometer bandpass, absorb their corresponding elements proportionately when present in the matrix.

It is necessary to recognize that the common method of background correction which uses a continuum source (H_2 or D_2 lamp) will fail with either spectral interference modes discussed above, as will calibration by the method of additions.

It is instructive to examine the work of Kelly and Moore[23] when determining zinc in iron meteorites by AAS. Figure 9 shows the absorbance of iron solutions using a zinc HCL at the zinc resonance line of 213.856 nm. Curve 1 shows slight curvature and represents the additive effects of background absorption and atomic absorption, while Curve 2 shows atomic absorption of iron only, after a deuterium continuum light corrector has subtracted background absorption. With the actual assaying conditions used, the spurious positive interference of iron is 15 μg Zn per 1 g Fe, and the authors concluded that iron should be removed from solution for a successful analysis.

However, the reviewer would suggest that it is not necessary to separate iron and zinc prior to AAS readings as suggested by Kelly and Moore.[23] Rather, the actual iron concentration in each assay could be simply determined using the same sample preparation and a suitable iron absorption line.[45] Then the gross zinc absorbance at zinc (213.856 nm) could be corrected for the actual iron and background absorption at 213.8 nm. Accordingly, the following generalized approach, which does not require preliminary separation for AAS determination of an analyte in the presence of spectral and/or background interference is suggested: measure the absorbance of the analyte at the resonance wavelength, measure the absorbance of interfering elements at the analyte resonance wavelength using the same flame and instrumental conditions used for the analyte, prepare concentration-absorbance calibration curves for each element which gives spurious absorbance at the analyte resonance wavelength, evaluate nonspecific background absorbance, and measure the actual concentration of offending interfering elements in the same solution prepared for the analyte. The actual concentration of the analyte can be calculated from the generated data.

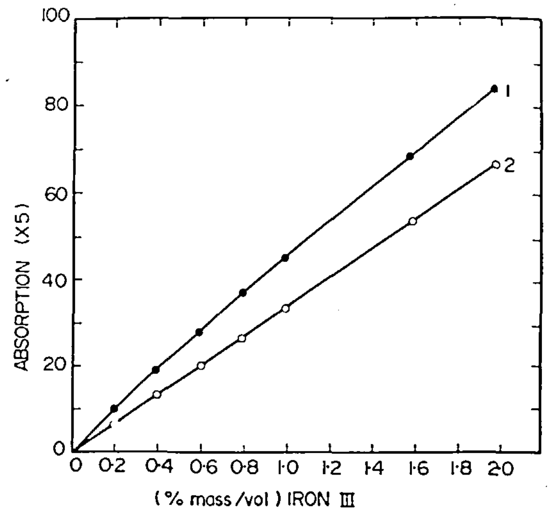


FIGURE 9. Absorption (scale expansion X 5) of iro (III) using zinc HCL without background correctio (Curve 1) with background correction (Curve 2). Wavelength set at the zinc resonance line 213.856 nm for a air-C_2H_2 flame. (Reprinted with permission from Kelly W. R. and Moore, C. B., *Anal. Chem.*, 45, 1274 (1973) Copyright by the American Chemical Society.)

Rains and Menis[22] recommend the technique of repetitive optical scanning to enable correction for the effects of overlapping bands resulting from matrix or flame components in AES. For the specific example of determining traces of aluminum in steel using 396.2 nm and N_2O-C_2H_2, a tenfold improvement in detection limit was achieved compared with the nonscanning mode.

Future workers will require an increased awareness of the various spectral interferences contributing to spurious analyses. An increased reporting of observed interferences and correction methods would be beneficial.

ii. Background Interference from Air-C_2H_2 Flames

The analysis of complex ferrous materials for trace elements gives rise to serious background correction problems.[96,108,109] Fortunately, a

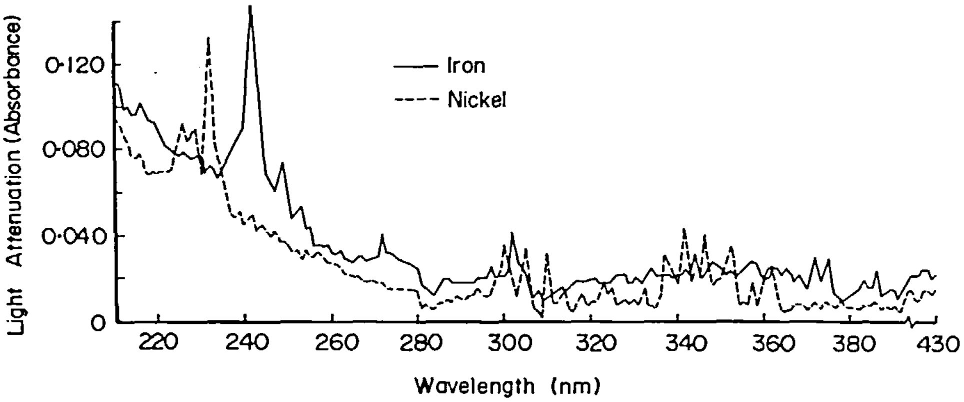


FIGURE 10. Light attenuation (absorbance) by 4% (mass/vol) iron and nickel as iron (III) and nickel (II) chlorides in air-C_2H_2 for the range 210 to 430 nm. (Reprinted with permission from Marks, J. V., Spellman, R. J., and Wysocke, B., *Anal. Chem.*, 48, 1474 (1976). Copyright by the American Chemical Society.)

number of serious workers have studied the nature of background interference in the air-C_2H_2 flame, a subject poorly understood by many workers. Marks et al.[108] emphasized that the measurement of and correction for background light losses set the lower concentration limits for accurate elemental determinations in flame AAS. Endo and Nakahara,[91] when making AAS measurements, defined background as all absorption phenomena due to iron matrix cations, solvent anions, and flames, even when the analyte is not present or below the limit of detection.

Marks et al.[108] determined the light attenuation (absorbance) of a continuum lamp by 4% (mass/vol) solutions of iron and nickel as iron (III) and nickel (II) chlorides in air-C_2H_2 for the range 210 to 430 nm. The results are shown in Figure 10. Quite clearly, nonspecific background absorption by iron is a significant problem (particularly in the region of 210 to 280 nm) and cannot be ignored when calculating the concentration of an analyte.

Additional aspects of attenuation with some accompanying spectral interference in the air-C_2H_2 flame have been graphically illustrated by Endo and Nakahara.[91] Figure 11 shows background attenuation and specific absorption in the vicinity of zinc (213.9 nm) by a 1% (mass/vol) iron (III) solution in the optical path of a zinc-copper HCL. Figure 12 shows severe background attenuation and lack of specific absorption in the vicinity of cobalt (240.7 nm) by a 1% (mass/vol) iron (III) solution in the optical

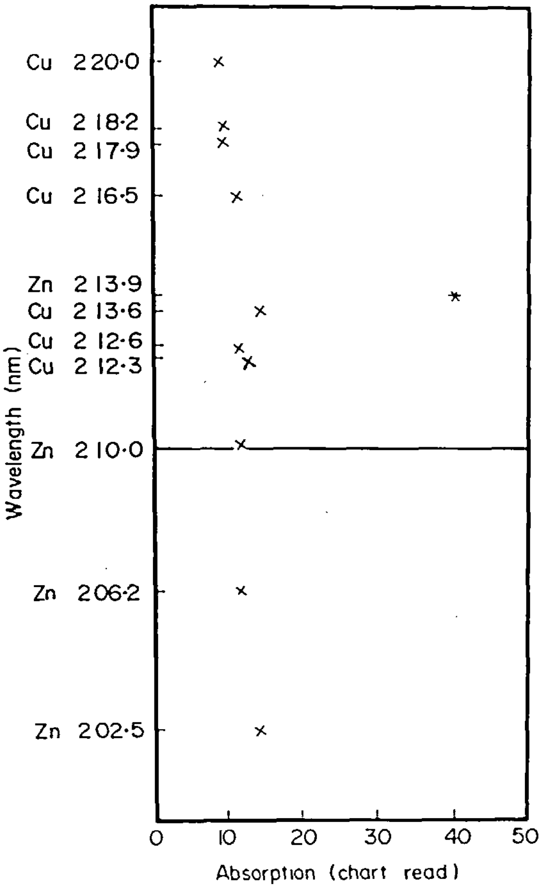


FIGURE 11. Background attenuation and specific absorption in air-C_2H_2 in the vicinity of zinc (213.9 nm) by 1% (mass/vol) iron (III) in the optical path of a zinc-copper HCL. (Reprinted from Endo, Y. and Nakahara, Y., *Tetsu To Hagane*, 59, 800 (1973). With permission.)

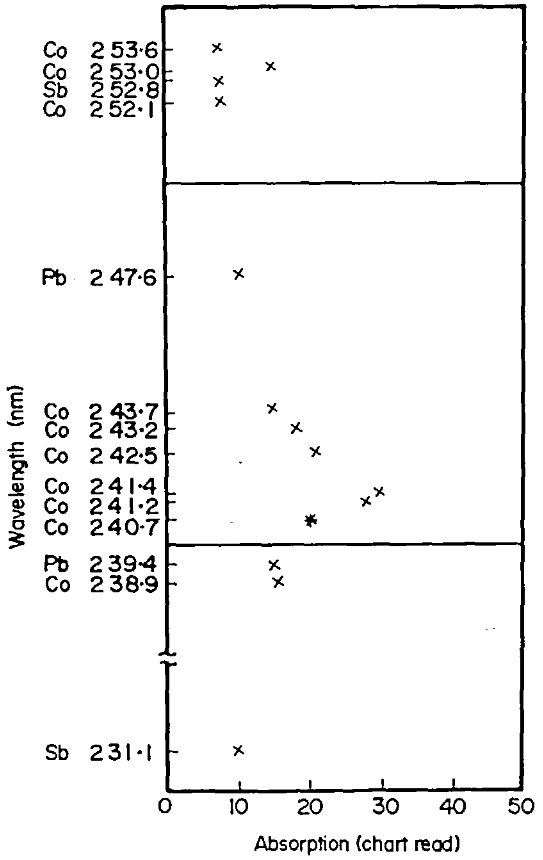


FIGURE 12. Severe background attenuation and lack of specific absorption in air-C_2H_2 in the vicinity of cobalt (240.7 nm) by 1% (mass/vol) iron (III) in the optical path of a cobalt HCL. (Reprinted from Endo, Y. and Nakahara, Y., *Tetsu To Hagane*, 59, 800 (1973). With permission.)

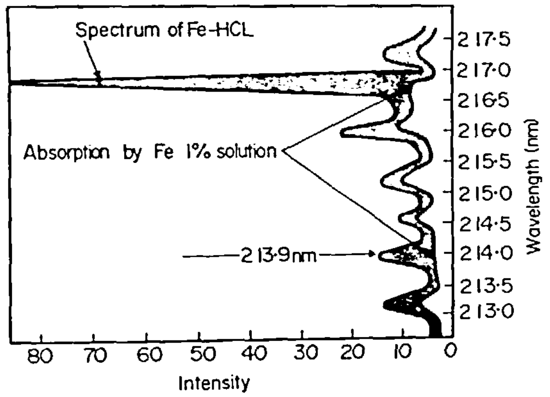


FIGURE 13. Specific absorptions in air-C_2H_2 in the vicinity of zinc (213.9 nm) by 1% (mass/vol) iron (III) in the optical path of an iron HCL. (Reprinted from Endo, Y. and Nakahara, Y., *Tetsu To Hagane*, 59, 800 (1973). With permission.)

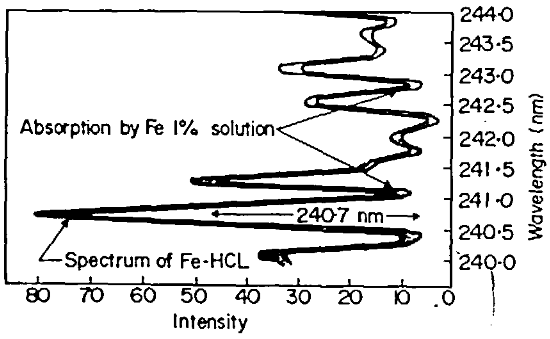


FIGURE 14. Lack of specific absorption in air-C_2H_2 in the vicinity of cobalt (240.7 nm) by 1% (mass/vol) iron (III) in the optical path of an iron HCL. (Reprinted from Endo, Y. and Nakahara, Y., *Tetsu To Hagane*, 59, 800 (1973). With permission.)

path of a cobalt HCL. Figure 13 shows specific absorptions in the vicinity of zinc (213.9 nm) by a 1% (mass/vol) iron (III) solution in the optical path of an iron HCL. Figure 14 shows the lack of specific absorptions in the vicinity of cobalt (240.7 nm) by a 1% (mass/vol) iron (III) solution in the optical path of an iron HCL.

It is useful to consider light attenuations in the vicinity of the cobalt (240.7 nm) resonance line. The attenuation of iron at 241 nm in the vicinity of cobalt (240.7 nm) supports earlier observations,[103] further indicating that attenuation varies with flame combustion conditions, being at a maximum in an oxidizing flame. Fleming[103] and Marks et al.[108] agree that this iron maximum attenuation peak is due to an FeO band; furthermore, there is nonspecific background absorption for which corrections are required. The attenuation of iron by spectral interference at zinc (213.9 nm) was discussed in Section IV.C.1.d.i.

A persistent feature of standard methods[34] and many published papers[10,110] covering the determination of major and minor analytes is a preoccupation with using only one set of calibration curves with a preferred concentration range. This technique has the undesirable feature of requiring deliberate additions of matrix solutions to diluted assays in order to return to a matrix concentration compatible with the calibration curves. Although this practice has the advantage of limiting the number of calibration standards to be prepared, the solids and solvent anion concentrations are kept unnecessarily high, which turn, maintains an unnecessarily high level of onspecific background absorption or spectral terference. Now that many of the interference atterns are understood in atomic spectrometry, it ould be desirable for analytical chemists to onsider using calibration standards and assays hich are as dilute as practicable.

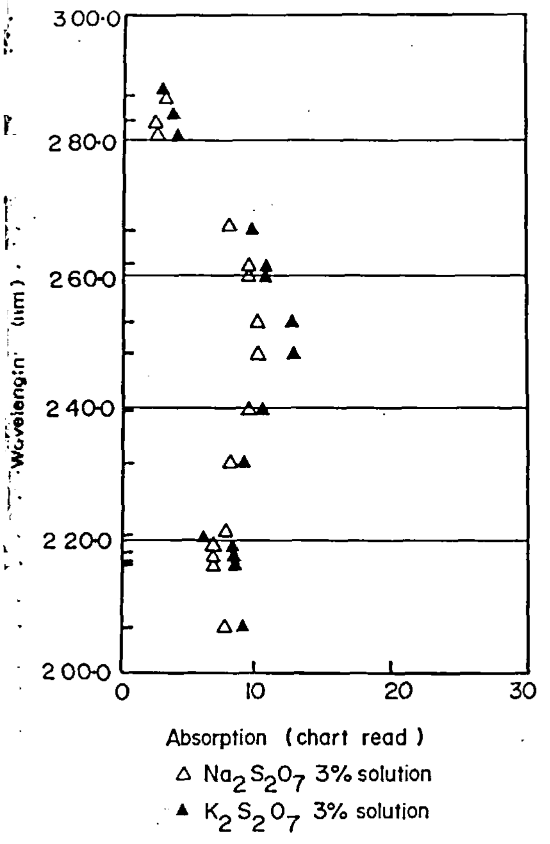
Endo and Nakahara[91] studied potential back-ound absorption with the air-C_2H_2 flame using parate 1.0% (mass/vol) solutions of Ca, Cr, Na, d K and 10% (v/v) solutions of HCl, HNO_3, ClO_4, H_2SO_4, and H_3PO_4 at selected wave-ngths in the range 205- to 280 nm. These lutions represent major associated matrix ele-ents, fusion agents, and acids.

Calcium and chromium background absorption as approximately twice the corresponding iron ckground absorption,[91] whereas nickel was milar to iron (Figure 10).

Both sodium and potassium caused absorption at 205 to 280 nm, as shown in Figure 15, and cannot be ignored in method and matrix design; however, the reviewer suggests that confirmation is required that this absorption pattern would be similar if, for example alkali carbonate fusions were considered together with neutralization with alternative anions, e.g., HCl.[91]

There is almost no absorption by hydrochloric acid and only minor absorption by nitric and perchloric acids in the range 205 to 230 nm, whereas for phosphoric and sulfuric acids (as shown in Figure 16) significant absorption is experienced for 205 to 280 nm, increasing directly as wavelength decreases. Accordingly, sulfuric and phosphoric acid concentrations must be well matched when preparing solutions of assays and standards.[91]

Concerning future studies, it is clear that the range and significance of specific and nonspecific



IGURE 15. Background absorption of 3% (mass/vol) $a_2S_2O_7$ and 3% (mass/vol) $K_2S_2O_7$ in air-C_2H_2 at 205 280 nm. (Reprinted from Endo, Y. and Nakahara, Y., *etsu To Hagane*, 59, 800 (1973). With permission.)

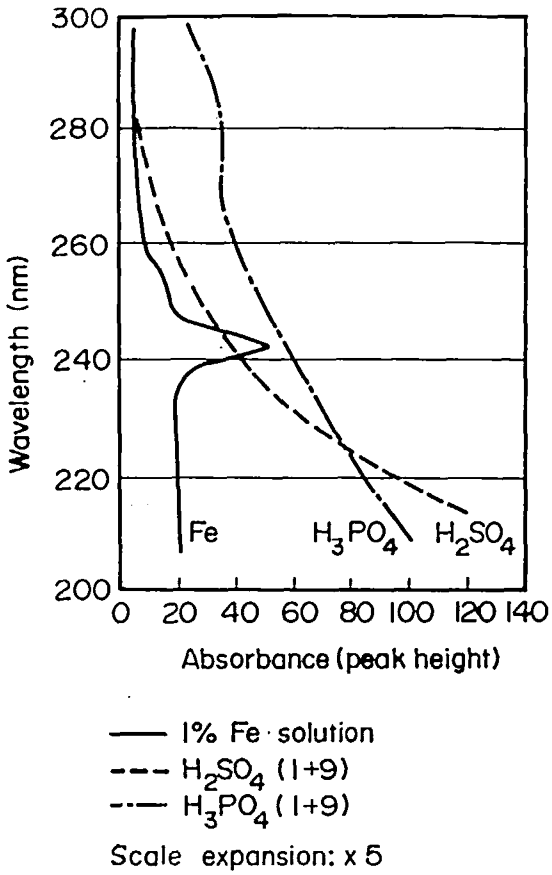


FIGURE 16. Background absorption of 10% (v/v) H_3PO_4 and 10% (v/v) H_2SO_4 in air-C_2H_2 at 210 to 300 nm. (Reprinted from Endo, Y. and Nakahara, Y., *Trans. Iron Steel Inst. Jpn.*, 16, 396 (1976). With permission.)

background absorptions have been adequately demonstrated by a number of workers. Future methods and standards should show full cognizance of background interference and incorporate suitable methods of minimizing the effect and achieving correction.

iii. Correction of Background Interference from Air-C_2H_2 Flames

Endo and Nakahara discussed the difficulty of analyzing minor amounts of Bi, Co, Cu, Ni, Pb, Sb, and Zn, particularly with respect to the level of matrix background absorption, and suggested that advantages were experienced by extracting iron before nebulization.[3] However, Marks et al.[108] concluded that the most accurate AAS background correction method uses blanks, which achieve complete matching with the composition of the samples to be analyzed (particularly with respect to the components which cause background light losses) and that the magnitude of background light losses may be significantly reduced but not eliminated by proper optimization of flame stoichiometry and measurement height in the optical path. Between these viewpoints, three background correction methods have been discussed, viz., pure iron, nearby line, and continuum light.[53,91]

The pure-iron method is a simpler variant of the complete matrix-matching method.[108] Endo and Nakahara[91] do not support the concept of complete matching, which, of course, requires that the concentration of any matrix element making a contribution to background or spectral interference be known. Hence, it was correctly concluded that the pure-iron method can fail for high-alloy steels and iron ores.[91]

The nearby line method is based on the observation that background absorptions change only slowly with varying wavelength, provided there is no spectral interference, cf., Figures 11, 15, and 16. Accordingly, background can be corrected using a line near the analyte resonance line, selected from the emission lines of the analyte lamp source or the enclosed gas. If the analyte lamp does not have a suitable nearby line, a line in another HCL may be used. The requirements of the nearby line technique are (1) the chosen wavelength must be nearby (<10 nm), (2) the intensity of the nearby line should be relatively similar to that of the analyte line, (3) the nearby line should be known and characterized, (4) the analyte should not absorb at the nearby line, (5) there should be no spectral interference by matrix elements at the analyte line, (6) the nearby line should not experience spectral interference by matrix elements, and (7) the readings must be obtained with exactly the same flame and general instrument settings as with the analyte.[91] This technique is supported by Thompson and Godden[53] who experienced severe difficulty when applying the continuum-light method to 10% (mass/vol) solutions used for pulse-nebulization techniques. The reviewer suggests the use of a separate spectrographically pure solution for each matrix element to prove the validity of selected nearby correction and analyte lines. Furthermore the possibility of interference by matrix elements from a transition not commencing in the ground state should not be overlooked when assessing possible interference by matrix elements on the nearby line.[108]

The continuum-light method is typically based on the use of hydrogen- or deuterium-continuum sources for the range 210 to 350 nm; more recently, Hg-Xe[111] and tungsten-continuum sources have been proposed to increase wavelength coverage. In many instances, either iron or major matrix elements have an absorption line occurring within the spectrometer bandpass of the continuum, and spurious background readings are experienced.[91,108] A typical example is the absorbance by iron (252.743, 252.913, and 252.983 nm) of antimony (252.853 nm).[9 Similarly, iron-matrix absorption was reporte at tin (286.3 nm) and aluminum (309.2 nm when nebulizing 10% (mass/vol) iron solutions.[5 Another source of potential difficulty is spectra interference by the elemental material used t fabricate the cathode holders in continuu sources.[108] However, the continuum-light metho has the advantage that the background can b automatically subtracted from the signal, thu minimizing the number of readings made. Pro vided that the individual background absorptio of any elements with lines within the bandpa of the spectrometer are evaluated, this metho may be successfully used.

It can be concluded that a rigorous study o any proposed analytical determination should sug gest the best background correction method fo each specific case. Certainly, the careless use o continuum-light background correctors can lead t incorrect results.

The use of background correction has been proposed for an ISO draft method for the determination of copper in iron ore, where it is stressed that background corrections are required for 0.003 to 0.010% copper when making AAS measurements at the Cu 324.7 nm line using air-C_2H_2 flame and 0.5% (mass/vol) solutions.[112]

TABLE 6

The AAS Analyte Resonance Lines, Nearby Correction Lines, and Limiting Concentration of Matrix Elements for Data in Table 7

Element	Analyte resonance line (nm)	Nearby correction line (nm)	Matrix element limit (mg/ml)[a]
Sb	217.6	Sb, 217.0	<10 Pb
Bi	223.1	Pb, 220.4	–
Cd	228.8	Sb, 231.1	<0.2 Sb
Ni	232.0	Sb, 231.1	<0.2 Sb, <200 Ni
Mn	279.5	Pb, 280.2	<5 Pb
Pb	283.3	Pb, 280.2	

[a] The limiting values for matrix element (mg/ml) can be converted to μg/g in the sample. Multiplication × 100.

Reprinted from Endo, Y. and Nakahara, Y., *Tetsu To Hagane*, 59, 800 (1973). With permission.

The serious extent of background interference is not realized by all workers, and it is instructive to consider the examples of AAS determination of minor elements given for an electrolytic iron powder and an Australian iron ore.[91] Table 6 lists the analyte resonance line, nearby correction line, and the limiting concentration of matrix elements in the iron or iron ore matrix for each chosen nearby line. Table 7 shows the uncorrected AAS results for electrolytic iron and iron ore and results corrected by the pure-iron matching (method A) and the nearby line (method B) techniques. It is immediately apparent that the corrected results can be significantly lower and that the concordance between the two methods of correction is very satisfying.

Further studies are required to elucidate and prove background correction procedures for complex alloys. Future published methods and standards should show full cognizance of the background correction methods required to obtain an accurate result.

TABLE 7

Uncorrected and Corrected AAS Results for Electrolytic Iron and Iron Ore Using Air-C_2H_2

		Found (μg/g)		
Sample	Element	Uncorrected	Corrected A[a]	Corrected B[b]
Electrolytic iron (10,000 μg/ml, Fe)	Ni	85	70	72
	Co	123	91	–
	Zn	64	50	–
	Cd	2	<1	<1
	Pb	30	<10	<10
	Bi	60	<10	<10
	Sb	80	<10	<10
Iron ore (6,000 μg/ml, Fe)	Ni	45	36	37
	Co	25	<2	–
	Zn	22	13	–
	Cd	2	<1	<1
	Pb	30	10	10
	Bi	30	<10	<10
	Sb	50	<10	<10

[a] Background corrected by pure-iron matching.

[b] Background corrected by nearby line method using conditions in Table 6.

Reprinted from Endo, Y. and Nakahara, Y., *Tetsu To Hagane*, 59, 800 (1973). With permission.

iv. Background Interference from N_2O-C_2H_2 Flames and Corrective Techniques

Endo and Nakahara[91] repeated their AAS study of potential background absorption for iron, major associated matrix elements, fusion agents, and acids for the N_2O-C_2H_2 flame. These studies did not disclose nonspecific absorption in the range 250 to 300 nm, although some slight absorption was experienced for 210 to 250 nm. With the elements usually analyzed in steel and iron ore at 210 to 300 nm using N_2O-C_2H_2, only tin (224.6 nm) would require some concern for background, unless, of course, spectral interferences were encountered.

These studies clearly support the recommendation in Section IV.C.1.c that relatively higher temperature N_2O-C_2H_2 flames (with required admixtures of nitrogen) are advantageous for the determination of a significant number of elements, particularly with respect to background interferences usually encountered with air-C_2H_2. Further confirmatory studies similar to that of Endo and Nakahara[3,91] are required for N_2O-C_2H_2, and the 0.60-nm slot burner head[53] would have the significant advantages of allowing the use of >1% (mass/vol) solutions, improved zone definition, and the achievement of an improved sensitivity in many instances.

Fassel et al.[12] discussed the measurement techniques available for the flame AES determination of analyte elements in steel and recommended the alternate recording of background signal from a pure-iron solution and total signal from the sample using integration over ten sampling periods and printing out background-corrected relative spectral line intensities. It seems necessary to point out that a 100% iron matrix is inadequate for high- and, in some instances, low-alloy steels and that the background matrix should contain the major alloying elements together with any minor element that may give an emission within the analyte or background bandpass of the spectrometer. Rains and Menis[22] recommended repetitive optical scanning, enabling correction for backgrounds resulting from matrix or flame components.

v. Suppression, Enhancement, and Corrective Agents

The first requirement for controlling suppression and enhancement effects is that the standards be similar in all respects to the samples and ensuring that similar pretreatments are given.[3,10,26,65,67,110] An interesting example of inability to match calibration and assay samples is provided by an observation of the formation of significant concentrations of ammonium anion from the nitrogen present in alloys dissolved with reducing conditions.[113] Since ammonium can suppress[113] or enhance[110,114] the absorption of various analytes (Mg, Mo, and Cr), the nitrogen content o alloys should be known.

(a) Alkali Elements

The air-C_2H_2 flame is used for the AAS determination of alkali elements in ferrous solutions. Cobb et al.[115] demonstrated the mutua enhancement interference of potassium and sodium when these elements are determined in iro ore; the effect of matrix element variations wa insignificant compared to mutual enhancement. A small improvement was achieved by the additio of 14 μg/ml lithium as the sulfate to the hydrochloric acid media. The reviewer suggests tha lithium chloride would be a more suitable salt fo addition, a substantial addition of lithium (say to 2 mg/ml) would correct mutual enhancement o alkali metals, and a lanthanum addition (e.g., mg/ml) would be beneficial in certain matrice where aluminum, sulfate, or phosphate is derive from the sample.

An AES method using air-C_2H_2 was propose for the determination of 0.1 to 50 μg/g sodiu potassium, lithium, and calcium in high-allo stainless steels.[116] All four analytes experience serious enhancement from five significant matri alloying elements (Fe, Cr, Ni, Mn, and Ti), eve though separations to low residual concentratio of approximately 0.1 mg/ml had been achieved. was disappointing to the reviewer that the elega separations used were not supported by a bett choice of conditions for the determinative stag The use of a 0.5 to 2 *M* acid concentration rath than pH 4 and ionization control agents such cesium, lanthanum, or strontium would have bee beneficial.

(b) Alkaline Earth Elements

Workers seem satisfied that either air-C_2H_2 N_2O-C_2H_2 flame can be successfully used for AA determinations of calcium and magnesium. F air-C_2H_2, strontium was used almost exclusive during the review period to overcome suppressi effects due to sulfate, silicate, ammonium, a aluminum,[3,33,113,117] with N_2O-C_2H_2, sodiu was used for ionization control.[40,118] Lanthanum is beneficial and is used for interference control in either flame type.[35,40]

(c) Manganese, Copper, Nickel, Cobalt, Chromium, and Molybdenum

When these elements are determined in a ferrous matrix, AAS may be best carried out with N_2O-C_2H_2 flame diluted as necessary with nitrogen (Section IV.C.1.c).

Many minor interferences with the AAS determination of manganese can be overcome by adequate matrix matching,[10,67,119] and N_2O-C_2H_2 flame is beneficial in avoiding or reducing interferences.[41,118] The commonly reported interference is depression by silicon in air-C_2H_2 flame although correction was achieved with 200 μg/ml calcium.[117]

Copper and nickel are not troubled by interferences, although the matrix should be matched.[119] Cobalt has been discussed in Section IV.C.1.c, where it was concluded that most difficulties experienced with AAS determinations are overcome by using relatively oxidizing N_2O-C_2H_2 flame.

The consensus view suggests that the most satisfactory AAS determination of chromium is achieved with the analyte in the trivalent state and the use of oxidizing N_2O-C_2H_2 flame.[3,10,20,67,106,114] The reduction of chromium (VI) to chromium (III) is best achieved with a mildly specific reducing agent, such as hydrogen peroxide,[14] because iron (II) causes serious interference.[43] On the other hand, it was proposed that a relatively rich air-C_2H_2 flame should be used so that an enhanced c_L can be achieved.[43,47,110] Under these conditions, 8 mg/ml of 8-hydroxyquinoline further enhances chromium sensitivity and controls the majority of interferences, excepting phosphate. Ammonium chloride, at a concentration of 10 to 20 mg/ml, is a useful releasing agent with either air-C_2H_2 or N_2O-C_2H_2 flame.[114,120]

Norris and West experienced severe depression by iron for the AFS determination of $< 0.05\%$ chromium in 0.02% (mass/vol) iron media with a separated air-C_2H_2 flame; this interference was overcome by solvent extraction of the iron.[121]

The AAS determination of molybdenum should be carried out with stoichiometric N_2O-C_2H_2. Typical releasing and ionization control agents are 100 μg/ml aluminum,[3] 1 mg/ml potassium,[106] and 10 mg/ml ammonium chloride.[110] Wada[122] attempted to use 3.2 mg/ml sodium with air-C_2H_2 flame, but could not overcome depressive interferences.

(d) Aluminum, Silicon, Vanadium, Tungsten, Titanium, and Niobium

These refractory elements can only be determined with N_2O-C_2H_2 flame, and, in most instances, a relatively fuel-rich flame is required to achieve absorption or emission.

Several workers have relied upon matrix matching without the use of an ionization control agent for the AAS[10,119,123] or AES[12] determinations of aluminum. This approach is not recommended because minor amounts of silicon and sodium will depress or enhance, respectively, the proportion of ground state atoms in the flame.[44,124] For AAS determinations, it has been proposed that 2 to 6 mg/ml potassium[14,117] or 1 to 7 mg/ml sodium[34,125] is suitable for ionization control and enhancement of aluminum absorption. However, silicon will depress aluminum absorption (even in the presence of sodium or potassium), and Cobb and Harrison[125] and Harrison et al.[124] found it necessary to use 2.0 and 1.2 mg/ml lanthanum, respectively, to overcome this interference. It should be appreciated that an opportunity to remove silicon is usually presented if a dehydration is carried out, followed by filtration, ignition, and volatilization as fluoride. For the AES determination of 0.01 to 100 μg/ml aluminum, Rains and Menis[22] proposed the use of 1 mg/ml potassium to avoid ionization interference and calibration line curvature.

Again, a number of operators have relied upon matrix matching without the use of ionization control for the AAS determination of silicon in steel[3,119,126,127] and iron ore.[118,128] However, as silicon is sensitive to enhancement and depression, this approach is not recommended. Rooney and Pratt[66] recommended 10 mg/ml sodium for ionization control when determining silicon in steel; likewise, Guest and Macpherson[129] used 6 mg/ml sodium for iron ore. Even so, interference was experienced from iron, copper, and lead, and matrix matching was recommended.

Interferences with the AAS determination of vanadium are extensive and have been studied in detail.[130,131] Increasing iron concentration continually depressed vanadium absorption; chromium and cobalt depressed[130] and molybdenum, aluminum, and manganese enhanced vanadium absorption, respectively.[130,131] Titanium has been reported to both depress and enhance.[130,131] Aluminum (1 mg/ml) and lanthanum (2 mg/ml) were both studied as control agents, with the best plateau and ionization controls achieved by aluminum.[130] Various workers almost invariably used aluminum in concentrations ranging from 100 to 3000 μg/ml.[3,28,30,31] Husler recommended 1 mg/ml potassium for high-alloy steel.[106]

Rooney and Pratt[66] recommended 10 mg/ml sodium, and Husler[106] recommended 1 mg/ml potassium for interference and ionization control when using hydrofluoric acid media for the AAS determination of tungsten. However, other workers relied upon matrix matching only when using phosphoric acid media.[10,126]

Thomerson and Price[10] find no interferences for the AAS determination of titanium in steel; however, Cobb et al.[132] studied the control of depression by lanthanum and aluminum and recommended 500 μg/ml aluminum because a plateau effect could not be established with lanthanum. Endo[3] recommended (500 μg/ml aluminum + 3 mg/ml potassium) for determinations in iron ore and 100 μg/ml aluminum for steel; also, 5 mg/ml aluminum was used to achieve a 170% enhancement of titanium absorption.[133]

For the AAS determination of niobium, Martin[134] reported that 5 mg/ml aluminum enabled a twofold enhancement of the absorption of niobium in tartaric acid media, whereas Thomerson[135] showed that a constant 2% (mass/vol) iron media achieved an enhancement plateau and that an ionization control agent was not required.

The relatively poor sensitivity of the refractory elements and the lack of universality of the control agents requires the following: the calibration standards and assays be closely matched, the calibration not be extended over major ranges of concentration, and the use of releasing or control agents. The limited analyte concentration range (within which an interference control plateau could be achieved) requires that cognizance be given to the concentration of any potential control agent already contained in the assay sample. Future studies should concentrate on the development of optimal flame compositions and temperatures in conjunction with the use of known releasing agents.

2. *Hydride Evolution*

Hydride evolution is a well-established technique of analytical chemistry. The recent resurgence in conjunction with AAS is due to the lower c_L values which can be achieved, the ability to remove the analyte from matrix interfering elements, and the achievement of a concentration effect without attendant contamination risks. Hydride evolution AAS allows the use of low-temperature flames, such as air-entrained Ar/H_2, having the significant advantage of absorbing much less radiation in the ultraviolet region than air-C_2H_2 or N_2O-C_2H_2. Equally advantageous is the alternative use of flameless externally heated absorption tubes. Sodium borohydride, because of speed of reduction and simplicity, has replaced other reductants for hydride generation. Fleming and Ide[58] have made the only extensive study of the application of hydride evolution AAS to ferrous metallurgical analysis.

a. Apparatus

The hydride evolution cells of recent design can deliver a pulse of hydride suitable for determination by AAS or AFS. A recent review provided a broad overview of general developments in apparatus and technique.[136]

The instrumentation shown schematically in Figure 17 was developed by Fleming and Ide[58] for minimal manipulations, minimal change in flame characteristics (as evolved hydride is introduced into the flame), and minimal modifications to conventional atomic spectrometers. The total hydrogen flow plus a portion of the argon flow were premixed after metering and passed into the burner chamber at the burner end of a conventional spray chamber. The remaining argon flow plus the gases generated in the cell were admitted through the nebulizer end of the spray chamber.

The demountable glass evolution cell shown in Figure 17 was designed for ease of cleaning, recharging, and observation of the stirring action. Since the top part of the cell is mounted in the gas line, the lower portion can be interchanged. In practice, several lower portions were used so that solutions could be prepared in batches. A pellet was preferred for the introduction of sodium borohydride reductant; accordingly, the orifice at the top of the cell was designed so that escaping argon gas supported the pellet until the cork stopper was pushed into the cell. It was claimed that this system of pellet introduction excluded air

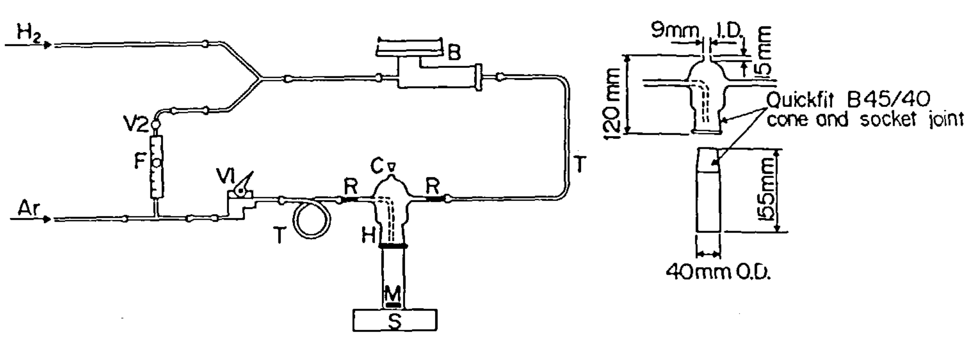


FIGURE 17. Schematic arrangement of hydride generation cell and associated gas lines. (B) Burner; (R) restriction (2 mm ID X 20 mm); (H) hydride generation cell; (M) magnetic stirring bar; (S) magnetic stirrer; (V1) on-off valve; (F) flow meter; (V2) regulating valve; (T) flexible tubing; (C) cork stopper. (Reprinted from Fleming, H. D. and Ide, R. G., *Anal. Chim. Acta,* 83, 67 (1976). With permission.)

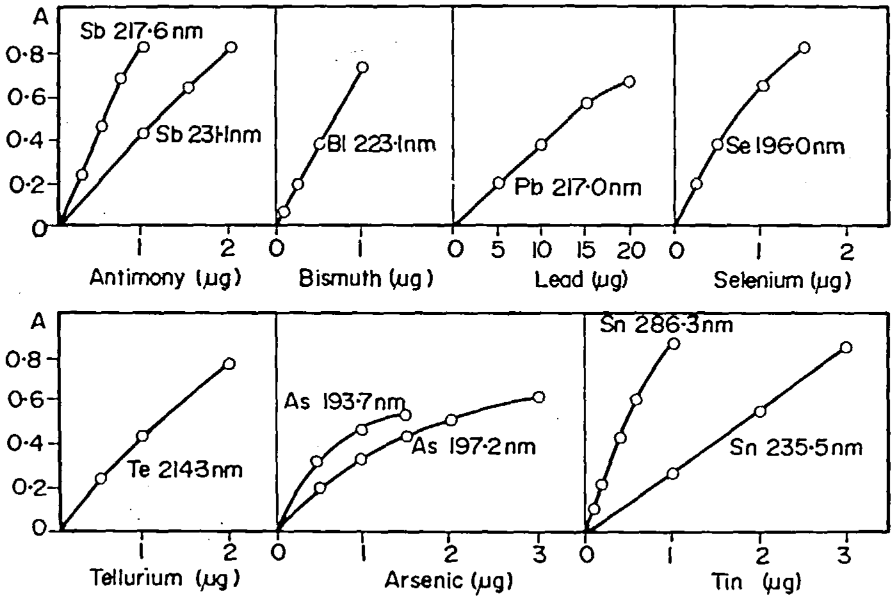


FIGURE 18. AAS calibration curves obtained for ferrous materials using hydride evolution. (Reprinted from Fleming, H. D. and Ide, R. G., *Anal. Chim. Acta,* 83, 67 (1976). With permission.)

from the cell. For all elements, the hydride evolution rate is to some extent dependent on the rate of stirring. As a result, precise results were obtained by using a constant and reproducible rate of stirring, which was relatively unaffected by the introduction of the sodium borohydride pellet. This was achieved by using a strong magnet and the largest stirring bar that would fit into the cell.[58]

Typical calibration curves obtained for the analysis of low- and high-alloy steels are shown in Figure 18. Samples of 20 mg were used in the cell; accordingly, a 1-µg analyte concentration in the cell is equivalent to 50 µg/g in the alloy, which (with the exception of lead) provides excellent sensitivity for ferrous materials.[58] The calibration curvature experienced for elements with the lowest wavelength resonance lines (selenium and arsenic) can be overcome by using a narrower slit (0.2 mm) or EDL. The c_L values are 1 µg/g for Sb, Bi, Se, Te, and As; 2 µg/g for Sn; and 7 µg/g for Pb.[58]

Some workers prefer the injection of a borohydride solution into the generation cell; others criticize this approach on the grounds that the injection rate cannot be precisely controlled from sample to sample.[78] However, Goulden and Brooksbank[138] pointed towards the direction of the future by proposing an automated apparatus based on a well-proven automatic analyzer system. Commmercial-automated hydride evolution apparatus has now been specifically designed for AAS, allowing a high rate of sample input with much improved reproducibility when compared to existing manual methods.

Externally heated 170-mm silica tubes of 8 and 3 mm in diameter were recommended as absorption tubes[15,78] rather than the conventional burner flame.[58] The tubes have the advantage of preventing ignition within the tube, thereby avoiding flame absorption background, particularly at wavelengths less than 200 nm. Also, the tubes provide a concentrated hydride gas density in both the longitudinal and transverse directions, as compared with conventional flames.

Hydride evolution is limited to a few gaseous-hydride elements, generally regarded as deleterious in ferrous materials, and improved c_L values of 0.05 μg/g will be required to satisfy future demands. Accordingly, some improvements in apparatus design and automation will be required to attain this goal. The relative merits of the conventional burner flame and the nonignited absorption tubes require comparison and assessment.

b. General Application

Fleming and Ide[58] transferred 2-ml aliquots (20 mg iron) to the hydride generation cell and optimized various reagents for the specific production of each hydride. The generation volumes were 10 or 15 ml, and the cell was vigorously stirred for all elements except lead. No significant background absorption was detected; consequently, whenever a spectrometer with two monochromators is available, two analytes can be simultaneously determined, provided the hydride generation conditions are compatible.

It was essential to maintain the iron concentration at 20 mg in the hydride generation cell, even when dilution was used or a highly alloyed steel analyzed. The effect of acid type and concentration on optimal hydride generation was discussed. Graphs of reagent concentration vs. absorbance were presented, and the acidity recommended for each analyte occurred in the region of maximum absorption. All curves showed a gentle change in absorption, with the exception of lead which rises rapidly to and falls from a peak at 3.8% (mass/vol) tartaric acid. For the optimal production of stibine, antimony should be in the trivalent state; this was achieved with a prior addition equivalent to 3.5% (mass/vol) potassium iodide. An addition equivalent to 1.5% (mass/vol) potassium iodide was recommended for tin whenever > 60 μg copper (> 0.3 mass%) was present in the cell. A prior addition equivalent to 2.2% (mass/vol) potassium dichromate was required for the generation of plumbane, whereby the reduction reaction was modified to allow hydride formation and release. A summary of the recommended conditions[58] for the generation of each individual elemental hydride is shown in Table 8.

The effect of solution volume in the cell on the efficiency of hydride generation (absorbance at fixed concentration) is shown in Figure 19. Apart from antimony and tin, the peak absorbance values for all elements decreased markedly with increasing generation volume. These observations support the design trends of recent apparatus, where the development of small volume cells[78,139,140] and high-speed reactions[58] has been pursued. Accordingly, the earlier bulb-[141] or cold-trap collection systems have been superseded.[83]

When appropriate standard reference materials were available, Fleming and Ide[58] achieved good agreement with certificated values or those proven by alternative techniques. They achieved relative standard deviation values which were similar to alternative techniques: 2, 4, and 7% for > 100, > 20, and < 10 μg/g, respectively.

In summary, the desirable trend to automation of hydride evolution and measurement will require variation of some of the conditions developed.[58] Studies are required to achieve simultaneous evolution of two or more analyte hydrides so that some repetitive aspects of the technique can be overcome. An improved supply of suitable standard reference materials is urgent. Extension to the analysis of iron ore should be achieved without difficulty.

c. Interferences

The majority of earlier literature on hydride evolution did not describe interference studies.[78,141] Several studies experienced difficulty with tin[139] and arsenic[78] impurities in sodium boro-

TABLE 8

Recommended Conditions for the Generation and Analysis of Evolved Elemental Hydrides in Ferrous Materials

Element	Generation media	Generation[a] volume (ml)	Analyte[b] in cell (μg)	Wavelength[c] (nm)
As	20% (v/v) HCl–2% (v/v) $HClO_4$	10	0–1	193.7
As	20% (v/v) HCl–2% (v/v) $HClO_4$	10	0–2	197.2
Sb	16% (v/v) H_2SO_4–1.5% (v/v) HCl–0.5% (v/v) HNO_3–3.5% (mass/vol) KI	15	0–1	217.6
Sb	16% (v/v) H_2SO_4–1.5% (v/v) HCl–0.5% (v/v) HNO_3–3.5% (mass/vol) KI	15	0–2	231.1
Bi	10% (v/v) H_2SO_4–2% (v/v) $HClO_4$	10	0–1	223.1
Pb	3.8% (mass/vol) $C_4H_6O_6$–2.2% (mass/vol) $K_2Cr_2O_7$ –2% (v/v) $HClO_4$	10	0–20	217.0
Se	17% (v/v) HCl–0.8% (v/v) HNO_3	10	0–1.5	196.0
Te	52% (v/v) HCl–0.8% (v/v) HNO_3	10	0–2	214.3
Sn	5% (mass/vol) $C_4H_6O_6$ – 1.5% (v/v) $HClO_4$	15	0–1	286.3
Sn	5% (mass/vol) $C_4H_6O_6$ – 1.5% (v/v) $HClO_4$	15	0–3	235.5

[a] Contains 20-mg iron.

[b] To convert μg of analyte to μg/g in ferrous material, multiply × 50.

[c] Burner height was 5 mm, and argon and hydrogen flow rates were both 6.0 l/min.

Extracted from Fleming, H. D. and Ide, R. G., *Anal. Chim. Acta,* 83, 67 (1976). With permission.

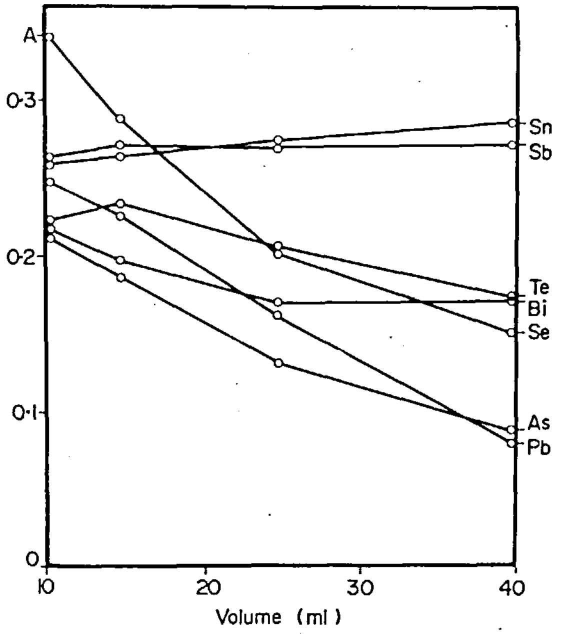


FIGURE 19. Variation of absorbance with hydride generation volume. Acid concentrations and additions as in Table 8. (Reprinted from Fleming, H. D. and Ide, R. G., *Anal. Chim. Acta,* 83, 67 (1976). With permission.)

hydride, although these difficulties are not reported in recent literature.

Smith[139] published a timely investigation of 48 potentially interfering elements studied separately at a level of 1 mg in the separate presence of 0.5 μg Bi, 1 μg As and Sb, 2 μg Se, and 10 μg Te at a fixed acidity of 1 *M* HCl with a generation volume of 13 ml. Two general conclusions were important: copper, silver, nickel, and cobalt always interfered, and the hydrides mainly cointerfered with each other. The suggested mode of interference was preferential reduction of the metal ion interference in solution to a different valency state or the free metal (which can cause precipitation and then either coprecipitate the analyte, adsorb or catalytically decompose the volatile hydride formed, or retard/prevent evolution from solution).

Belcher et al.[140] found several disagreements with Smith[139] and suggested the use of 0.01 *M* ethylenedinitrilo tetraacetic acid (EDTA) media, which almost eliminated interferences due to adsorptive or reactive capture of hydrides. Also, EDTA significantly reduced the extent of visible precipitation in the cell.

Fleming and Ide[58] alone faced the problem of determining hydride-forming elements in an iron matrix, whereas all earlier work studied simple solutions free from a dominant matrix. Although previous studies were valuable in defining the type of interferences encountered, there are significant differences between the recommended conditions for hydride generation given by other workers and by Fleming and Ide.[58] Generally speaking, the iron matrix did not affect sensitivity; in many instances, the presence of iron partially or completely overcame interferences which otherwise occurred. Fleming and Ide[58] opted for a fixed-iron concentration of 20 mg in the cell; however, it would have been instructive if minor iron variations consistent with known alloy types had been examined. Potentially interfering alloy elements were individually checked at levels equivalent to 20 Cr, 10 Ni, and 2.5 Mo, Co, Cu, Mn, and V mass%. A defect in the experimental design was an apparent failure to study these elements in common alloying proportions. Also, no study was made of possible cointerference of the hydride-forming elements. Nevertheless, a number of interferences were encountered, and, since there is no general pattern, these are discussed under the determination of the specific elements in Section VI.

Further studies are required to optimize the conditions for the generation and release of hydride-forming elements in ferrous materials. It is certain that a major impediment is the formation of precipitates during reduction; these either adsorb or form an intermetallic with the analyte. These studies should also define the role of interfering matrix elements which do not form precipitates, but which, nevertheless, either impede the rate of release of the hydride or partially prevent release. A study of the potential cointerference of the hydride-forming elements is imperative.

3. *Electrothermal Atomization*

Flameless electrothermal atomization techniques now engage the attention of many analytical chemists, as the prospect of achieving analyses in the range 0.01 to 10 μg/g with relative standard deviation values of 2 to 10% is highly attractive.[47] Rapid advances in the techniques have outstripped the availability of standard reference materials and pure metals, and deficiencies have been disclosed in hitherto acceptable reagents, laboratory atmospheres, and preparative vessels. Significant advances have been made with instrumentation; however, the development pace is such that further strides forward can be anticipated.

Earlier models of electrothermal GF atomizers were unsuitable for the analysis of iron-dominated matrices, but the present level of instrumental development and technique "know-how" has disclosed an exciting potential. While initial development was confined to AAS, the GF technique may now be applied to AES, and some exciting prospects for metallurgical analyses have been indicated.[4,47,50]

A coupled development of significance is the commercial availability of an automated device which can deliver an uncontaminated sample to electrothermal atomizers with a relative standard deviation of 1%, which is unachievable by manual operation.[142] Accordingly, the entire process can now be treated virtually as an unattended operation. This is a substantial improvement when compared with Hofton[77] who required four successive manual aliquots to obtain a mean result of significance.

The filament electrothermal atomization technique has not enjoyed significant application for ferrous matrices, and c_L, interferences, and precision achieved are not competitive with furnace techniques[8,143] and will not be discussed.

a. Apparatus

The electrothermal graphite rod or tube furnace atomization techniques have been developing in the present commercial forms since the beginning of the decade. With the technique, a small graphite rod or tube furnace is electrically heated through drying and ashing stages to a temperature where atomic vapor of the sample is formed in the optical light path. A comprehensive review of furnaces, injection, and atomization methods has been provided.[136]

The essential advantages of the technique are small sample volumes of 1 to 100 μl are used; small sample masses (10 to 500 μg Fe), typically, 100 to 1000 times less than with flame nebulization, can be atomized with high efficiency; little ionization occurs in the graphite atomizer, and, accordingly, ionization interferences are insignificant when compared with flame nebulization; the c_L values are 50 to 100 times better than with flame nebulization due to the relative absence of oxygen in the furnace and complete atomization of all the sample; and the analyte atoms stay in the optical path for a relatively long period of time (1 to 5 sec).[4,15,19,47,76,82,144-146]

Lundgren et al.[147] and Frech and co-workers[17,148-150] made a series of studies which could contribute significant improvements to present

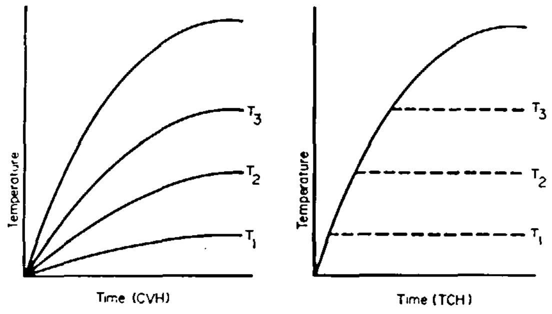


FIGURE 20. Schematic diagrams of heating profile as a function of time to achieve three final temperatures of T_1, T_2, or T_3 using either CVH or TCH. (Reprinted with permission from Lundgren, G., Lundmark, L., and Johansson, G., *Anal. Chem.*, 46, 1028 (1974). Copyright by the American Chemical Society.)

commercial apparatus. Furthermore, these studies have increased the potential for application to ferrous materials, particularly when temperature-controlled heating (TCH) of the GF is used.

Commercial GFAAS instruments are heated by a constant voltage applied to the tube or rod, and the temperature increases with time until heat losses balance the input power. Thus, Figure 20 shows a typical heating profile obtained with constant voltage heating (CVH) to three final atomization temperatures of T_1, T_2, and T_3. The three final temperatures and the corresponding heating rates are selected by tuning a variable transformer. The settings are variable, so that the operator can determine optimum parameters for each determination. Later commercial units have a "ramp" mode, which allows the temperature gradient to be set; however, rapid atomization cannot be simultaneously obtained with a low final temperature. Alternatively, the TCH method[147] shown in Figure 20 allows the temperature to rise rapidly until the preselected atomization temperature is reached; the power is then controlled to maintain this temperature. Thus, the heating rate and the final temperature, monitored by an infrared sensitive detector, can be independently set. The rod or tube can be rapidly heated to any predetermined atomization temperature between 750 to 2000°C and then maintained constant (± 10°C).

With CVH, a compromise is made between the required rate of atomization for a maximum signal peak and earlier diffusion losses, whereas with TCH, early diffusion losses are insignificant and atomization is mainly achieved at the most suitable isothermal temperature. Consequently, it is common to note that the temperature settings for maximum atomization for the two heating methods may vary by as much as 1000°C. Thus, for the example of lead in Figure 21, the furnace with TCH experiences a rapid increase of absorption starting at 950°C, and, with further small increases in the isothermal temperature setting, a constant absorption signal is obtained at $\geqslant$ 1060°C, whereas with CVH, a constant absorption signal is not obtained until a setting of $>$ 2000°C is used. The ratio difference (approximately 3:1 per nanogram) between the maximum absorbances achieved is notable. Of course, the CVH setting of $>$ 2000°C represents the final temperature, and, although the peak absorption will appear before this temperature is reached, it is evident that at least 66% of the available lead does not contribute to measured absorption.[147]

Frech[148] shows that lead losses in chloride media are caused by the fact that the CVH technique requires the use of an unnecessarily high temperature. Frech, when determining bismuth in ferrous materials, also confirmed the advantage of TCH, whereby the peak of maximum absorbance increases as a function of heating rate to the atomization temperature; a maximum absorbance was achieved with the maximum heating rate of 900°C/sec.[17] Frech showed that the degree of interference of matrix elements decreased significantly as the heating rate was increased to a maximum.[17,148,151]

Nonselective absorption increases as a function of furnace temperature, and it is clear that the background at maximum absorption signal is significantly higher for CVH as compared with TCH. Indeed, there is evidence that nonspecific background absorbance often exceeds the level which can be reliably handled with automatic background correctors. Clearly, TCH, with the ability to achieve a defined heating rate and constant operating temperature, sets a minimum standard of instrumental specifications for evaluating reactions and physical effects in GFAAS.[147]

Interferences due to molecular absorption and/or scatter in electrothermal GF techniques are a much greater problem than with flame nebulization, and simultaneous background correction is essential for precise and accurate analyses. Hydrogen and deuterium lamp sources are used as primary continuum sources (usually in a HCL form), but these provide inadequate visible radiant

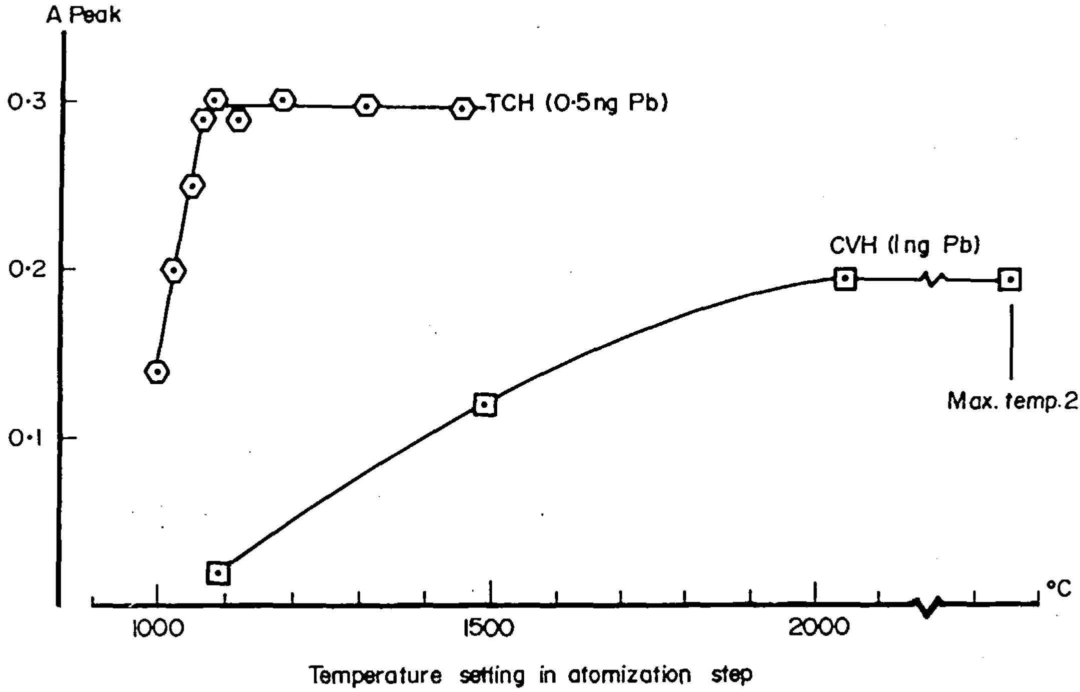


FIGURE 21. Comparison between TCH (0.5 ng Pb) and CVH (1 ng Pb) with respect to temperature settings for obtaining constant absorbance and the resultant maximum absorbances achieved. (Reprinted with permission from Lundgren, G., Lundmark, L., and Johansson, G., *Anal. Chem.*, 46, 1031 (1974). Copyright by the American Chemical Society.)

intensity to permit satisfactory balancing of intensities when operated at optimum amperages.

Most manufacturers of atomic spectrometers have been unwilling to provide a background correction lamp for the visible region. However, Epstein and Rains[111] have shown that furnace emission is quite severe for elements such as calcium, barium, and chromium, all requiring atomization temperatures of 2500 to 2700°C. The resonance lines of these elements occur in the visible or near-visible spectral region (where black-body radiation from the furnace is intense), and the output intensities of deuterium and hydrogen lamps are relatively low. Recently, one manufacturer has incorporated two background correction lamps into a single spectrometer, a deuterium lamp being used for the ultraviolet region and tungsten for the visible.

However, a viable, more versatile correction technique is the xenon-mercury arc lamp which provides adequate radiation intensity from 190 to 600 nm, except at 253.7 nm where the radiation is strongly self-absorbed by mercury vapor in the lamp.[111] A relative comparison of the radiant intensities of a hydrogen (H_2) HCL at 40 mA, a 25-W deuterium (D_2) arc lamp at 800 mA, and a 150-W xenon-mercury (Xe-Hg) arc lamp is shown in Figure 22. The xenon-mercury lamp is shown to be completely adequate for background correction in the ultraviolet and superior to a deuterium arc lamp in the visible region. A potential limitation of the xenon-mercury lamp at < 220 nm is the physical difficulties with stray light and spectral interferences; however, experimentation showed these to be minimal.

Adams and Kirkbright[152] have described a small graphite tube atomizer system enclosed within a nitrogen-purged optical path and used in conjunction with a vacuum monochromator. The unit was developed for AAS sulfur determinations at 180.7 nm. The main limitation was the lack of the necessary correction optics for nonspecific background. The achieved sensitivity for sulfur was 0.42 ng, suggesting potential development for the direct determination of sulfur and phosphorus in ferrous materials.

Attention has been drawn to the possibility of using an electrothermal GF in the AES mode.[4,47,50] Experimentation was carried out with a Perkin-Elmer Model 306 atomic spectrometer

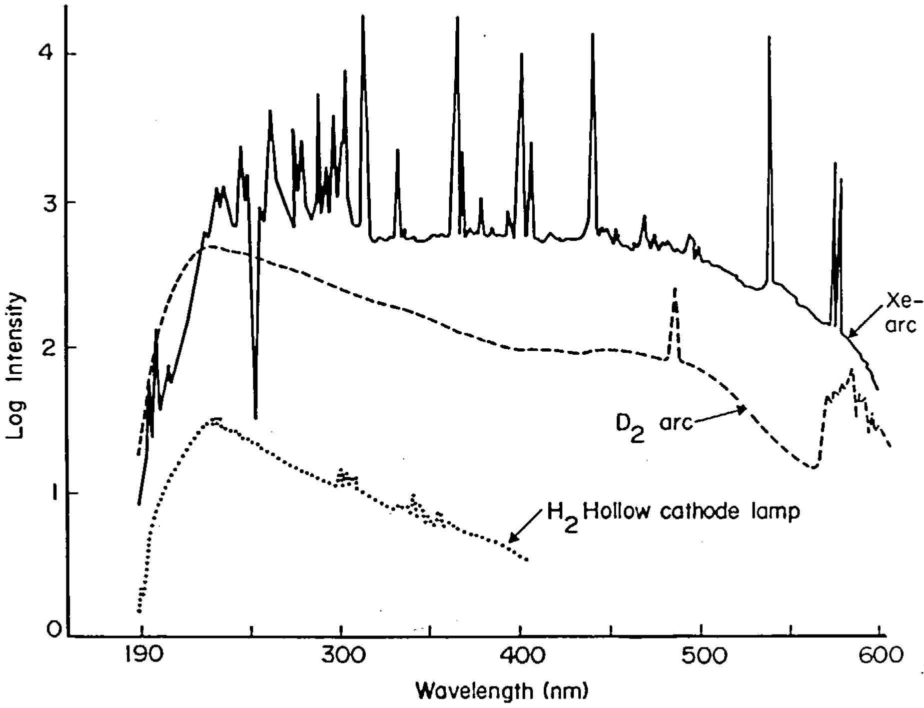


FIGURE 22. Comparison of relative intensities of three continuum lamp sources. (Reprinted with permission from Epstein, M. S. and Rains, T. C., *Anal. Chem.*, 48, 528 (1976). Copyright by the American Chemical Society.)

equipped with a HGA 72 furnace and strip chart recorder. The spectrometer required adjustable diaphragms to prevent excessive pickup of emission, particularly severe in the visible region, from the walls of the tube furnace. The c_L achieved with alkalis showed significantly better sensitivity (ten times) than achieved with the AAS mode, and when furnaces can achieve higher maximum temperatures, improved c_L will be achieved for the nonalkali elements, which, of course, require a higher excitation energy. This prediction has been demonstrated by reducing the wall thickness at the center of regular tubes.[47]

Unique applications to nonferrous metallurgy were reported, and application to ferrous metallurgy is predicted.[50] The elapsed time for the appearance of the emission and absorption peak signals was compared: the emission maxima occurred at a time interval 130% that of the absorption maximum. The purge gas was stopped during atomization to increase the residence time of atoms in the furnace. The emission signals are so transient that it is necessary to set the wavelength precisely by using an appropriate HCL. Background is determined by using a matrix-matched solution (not containing the analytes), and the analyte and background signals are alternately determined and subtracted to give net emission.

The future development of electrothermal GF technique is almost entirely dependent on the availability of improved apparatus. The AAS studies by Lundgren et al.[147] and Frech and co-workers[17,148-150] showed that further significant improvements are required in commercial electrothermal GF in order to meet the exigencies imposed by ferrous materials. Specific requirements are rapid heating rates of ≥900°C/sec with uniform temperature profiles and isothermal heating at desired temperatures to give absorption maxima, background minima, and minimum interference by matrix elements. A complete wavelength coverage by background correction lamps of sufficient intensity is required, and the xenon-mercury lamp requires serious consideration by manufacturers.[111] There is a challenge to develop apparatus for use at wavelengths < 190 nm, and the first model has been provided.[152] Ottaway and Shaw[4] are enthusiastic about the AES mode of the technique, and some special applicability to alkalis has been indicated but not yet proved for ferrous materials.

b. General Application

The previous discussion showed that much of the application technique described in the literature must be regarded as evolutionary in a rapidly developing field. Thus, the many conclusions regarding the efficacy of a particular acid media, the most suitable atomization and temperature profiles, and mutual interference of matrix and analyte must be judged against the limitations of the furnace used.

Frech and Cedergren[149,150] have emphasized the necessity of having a uniform temperature across the furnace tube or rod when the temperature is rising, particularly during the drying, ashing, and atomization isothermal periods. It was further indicated that the various reactions must be allowed to proceed to completion at each isothermal stage before the next heating stage commences. Furthermore, Frech[17,148] and Ottaway and Shaw[4] stressed the necessity of removing all possible material by including a short heating stage (postatomization if necessary) at the maximum temperature of the furnace in order to remove all potential interferents with the subsequent assay. Thus, Frech[148] quoted the necessity of removing molybdenum at the maximum temperature; otherwise, interference was experienced with the next AAS assay for lead. Ottaway and Shaw[4] were able to overcome spuriously high-background readings for the AES mode when alternately atomizing analyte-containing and analyte-free matrices.

.With respect to the ashing stage, many workers have referred to severe interferences and volatility in the AAS mode when hydrochloric acid medium is used.[19,47,77,153-156] Frech made the significant observation that hydrogen must be present during the ashing stage if difficulty is to be avoided with hydrochloric acid media.[148] Accordingly, since chloride is an important anion media in analytical chemistry and because of the conflicting views of various workers, Frech and Cedergren[149,150] described two theoretical studies of chloride interference in AAS tube and rod furnace technique, with special reference to the determination of lead in steel. The studies represent a watershed in an understanding of certain aspects of the ashing phase and virtually render obsolete the majority of existing commercial equipment, when considered in the context of applicability to the analysis of ferrous materials.

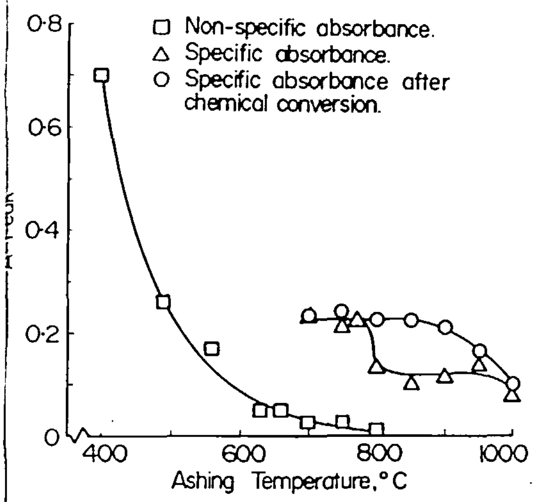
High-temperature equilibrium calculations were applied to a system containing Fe, Pb, C, Cl, S, H, O, N, and Ar. The results indicated that a sample must be ashed in the presence of a sufficient concentration of hydrogen and at a temperature not less than 630°C (in order to remove chlorine from a GF); otherwise, volatile lead chlorides ($PbCl_2$ and PbCl) are formed. The second matter of importance to emerge was the necessity of applying rapid heating from drying temperature to 630°C; otherwise, the same volatile lead chlorides can be formed.[149,150]

Frech and Cedergren,[150] having proved the necessity for the presence of hydrogen to remove chlorine by the reaction

$$FeCl_2(g) + H_2(g) \rightarrow Fe(s) + 2\,HCl(g)$$

found a disturbing variability between the ability of the Perkin-Elmer Model HGA72 and Varian-Techtron Model CRA GF to generate and supply the required hydrogen. Both systems generate hydrogen at high temperatures by the reaction of graphite with residual water in the tube or rod after the drying step. However, the HGA72 system generated approximately five times more hydrogen than the CRA unit, the former being sufficient to avoid the necessity for a separate hydrogen supply during the ashing step. Furthermore, it was shown that the CRA unit is adequate when an external source of hydrogen was supplied. It was also shown that at 430°C, all chlorine is not removed even if the hydrogen supply is adequate and that volatile lead chlorides are formed. The theoretically predicted optimum ashing range of 630 to 730°C was in good agreement with an observed 630°C.

The production of hydrogen by the reaction between water and graphite has apparently not been previously considered in GFAAS. Since hydrogen is always present during determinations in GF, then the concentration is obviously dependent on the type and amount of graphite used, the aliquot volume, and the condition of the graphite.[149,150] The porosity of the graphite normally tends to increase during a series of determinations, so that the concentration of residual water after the drying step will also increase. An increased concentration of hydrogen will be formed as the series proceeds; accordingly, the reproducibility of determinations across a series is unsatis-



IGURE 23. The overlap of nonspecific and specific sorbance caused by bismuth volatility. Following emical conversion with ammonia, a definite separation achieved and 880°C was chosen for ashing without latility losses. (Reprinted from Frech, W., *Z. Anal. hem.*, 275, 353 (1973). With permission.)

ctory. It is reasonable to assume that hydrogen ncentration is important for analytes other than ad.[150]

Further support for the role of hydrogen and rbon comes from innovative studies which condered that the thermal destruction of sample lutions in aqueous media should be carried out the presence of a water-soluble organic chemil.[157] It was proposed that the organic would roduce a "molecular mixture" of carbon and mple, assisting the efficient formation of atomic por and achieving a substantial removal of terelemental interference effects. Separate additions giving 1% (mass/vol) media of ascorbic acid, rtaric acid, or sucrose, were made to singleement solutions of 0.1 μg/ml lead, 0.02 μg/ml pper, or 1.0 μg/ml gallium in either 0.1% (v/v) ydrochloric or nitric acids. Significant enhanceents of absorption peak height and area were chieved. Ascorbic acid provided the maximum nhancement factors: 1.4 for lead, 2.0 for copper, nd 20 for gallium; furthermore, known suppresons were overcome. Nall confirmed the effectivess of ascorbic acid when applied to ferrous aterials.[15] The reviewer sees merit in the supply primary active carbon intimately mixed with mple as distinct from the normal tube or rod pply, and continuing studies will elucidate the omised advantages. Furthermore, the erosion te of the tube or rod should be reduced.

Several workers[19,47,77] have recommended oxyanion acids because of difficulties with hydrochloric acid. Ottaway[19] discussed the role of carbon as reductant, pointing out that oxyanion salts invariably break down into metal oxides and that the most likely atomization reaction will be reduction of the metal oxide by carbon, giving metallic species and carbon monoxide. While the oxyanion acids have been successfully used, a number of experimental precautions are required: ashing times have to be generally extended when sulfuric acid media are used,[77] an ashing stage is required when perchloric acid media are used (so that explosion-ejection losses will not occur),[158] and an argon flow is essential in overcoming the effect of available oxygen from nitric acid media and atmospheric oxygen.[151]

The determination of bismuth in steel by GFAAS provided an interesting example of the partial overlap of nonspecific absorbance caused by volatility losses prior to the atomization-absorbance sequence. This interference and the use of chemical conversion with ammonia processing to overcome the volatility loss are illustrated in Figure 23. Chemical conversion is extensively used in other fields, and extension can be expected for ferrous materials. Once improvements in instrumentation are achieved (as suggested in Section IV.C.3.a), chemical conversion should emerge as an effective method of avoiding sequence overlap.

Frech has emphasized the necessity of controlling the inert gas flow rate during the ashing cycle, even when analyte volatility losses are not occurring.[17] The concentration of oxygen (and therefore carbon monoxide) changes, affecting transformation during ashing and, hence, sensitivity. For the example of AAS determination of bismuth in steel, the peak absorbance declines as the inert gas flow rate increases (as shown in Figure 24); accordingly, the flow rates must be carefully controlled, and 50 ml/min was recommended.

Commercial instrumentation now features an "interrupt gas flow" facility which is commonly employed during the atomization cycle. Although the oxidation rate of the rod or tube is increased, the residence time and, consequently, peak absorbance are increased.[17,148]

Electrothermal furnace atomization is the most exciting and developing technique discussed in this review, although many challenges remain to be solved. The availability of fully automated equipment will have a strong influence on future

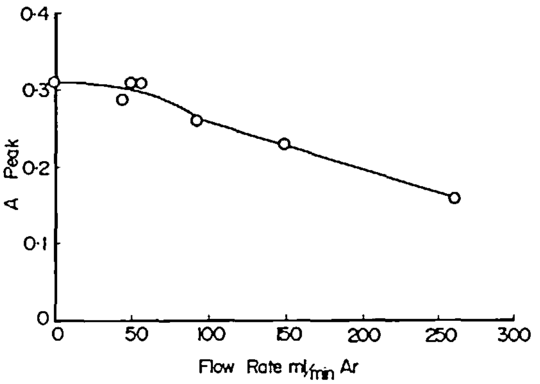


FIGURE 24. Peak absorbance of bismuth in steel as a function of inert gas flow rate during ashing. No gas flow during atomization. (Reprinted from Frech, W., *Z. Anal. Chem.*, 275, 353 (1975). With permission.)

developments. Workers will have to overcome some present problems posed by the lack of suitable standard reference materials, pure materials, reagents of inadequate purity, and the relative cleanliness of laboratory atmospheres. Much of the earlier work can be seen as evolutionary, but a number of promising lines of development have been indicated. The guidelines, providing for an understanding of the role of hydrogen[148] and hydrochloric acid,[149,150] need to be verified for other components. Regan and Warren[157] have attached importance to the provision of intimately mixed analyte and active carbon through the deliberate addition of organics, and, if found universally applicable, then a new dimension will have been added for control and reproducibility of reactions. Chemical conversion reactions could assume more importance when overlapping sequence reactions are encountered.

4. Indirect Analyte Analysis

An extensive review of indirect analyte methods for AAS listed five specific classes of procedures.[159] In each procedure, the analyte undergoes a reaction with one or more other ions, and the concentration, either of the reaction product or the unreacted excess of added reagent (directly or indirectly proportional, respectively, to the concentration of the analyte species in the sample) is measured. The authors emphasized the opportunities afforded by indirect methods: to improve sensitivity by analyzing a more sensitive element or by multiplying effects (e.g., heteropoly acids) or to improve accuracies by analyzing a residual unreacted species.[159] The basic limita tion, minimizing application to ferrous metallurgi cal materials, is the relative inability to arrang specificity of the initial analyte reaction.

An indirect technique which has been applie to steel is the formation of phospho-12-molybdi acid in 1.5 *M* perchloric[160] or 1.2 *M* nitric[16 acid media. A specific extraction with isobuty acetate is required to avoid interference fro arseno-12-molybdic acid and excess molybdat anion. Apart from ensuring specificity of reactio care is required to ensure that excess or adheri molybdate is washed from the separating funn and the butyl acetate layer. The development this method is occasioned by the absence suitable resonance lines of phosphorus at > 19 nm.[160,161]

Apart from the usual losses of phosphorus b occlusion with hydrolyzed tungsten and niobiu vanadium (V) interferes by consuming molybda to form a nonextractable heteropoly vanad phospho-molybdic acid. Titanium exceeding 0 mg causes interference by disturbing the 12/ stoichiometry of Mo to P.[160] Accordingly, con derable care is required to manipulate expe mental conditions if bias is to be avoided, and t indirect technique experiences all the hazards of nonspecific molecular spectrophotometric meth of analysis. Only limited specific purpose dev opment can be predicted for ferrous metallurgic analysis.

V. SAMPLE DISSOLUTION AND PREPARATION TECHNIQUES

A. General

The precision and accuracy attainable f atomic spectrometric analyses of ferrous materi depend critically on the attention given to initi sample collection and dissolution. However, t literature of atomic spectrometry scarcely includ observations on sample selection and dissolutio Accordingly, analytical chemists are referred appropriate national standards which discu sample collection and preparation[162-165] and specific discussions of dissolution difficulties.[24]

The direct sampling and atomization metho discussed in Section IV.B require simple samp preparation methods which are discussed mu too briefly in the various papers. However, as th methods develop, some specific difficulties w arise, including those which are well known multichannel spectrometric methods: metallurgical history, surface smearing by softer phases, preferential sputtering or arcing removal of nonmetallic phases, and surface contamination by surfacing abrasives.

Specific aspects of dissolution of alloys and oxides and various separation and concentration techniques will be reviewed in this section. No attempt is made to give specific details, and emphasis is given to the advantages and limitations of each technique.

B. Dissolution Procedures

Rigorous sample dissolution procedures are required to achieve the ultimate potential of atomic spectrometric solution methods of analyses. The required considerations include: the choice of solvent or flux; the existence of insoluble residues; interference by coexisting elements; the analyte element may gelatinize, volatilize, or hydrolyze on dissolution; contamination by laboratory vessels or atmosphere; encapsulation of inclusions and nonmetallics by partly hydrolyzed products before solution is achieved; and failure to consider residual or alloying concentrations of silicon as potential interference in dissolution procedures which do not remove this element.[3,24,112,166]

For quality work, there is a trend away from traditional borosilicate glassware to polytetrafluoroethylene (PTFE) or platinum wares to resolve samples and carry out subsequent concentrations and separations. The advantages include relative freedom from analyte elements and the ability to carry out dissolutions with hydrofluoric acid or alkaline solutions.

The hydrolysis and dehydration behaviors of Si, W, Mo, Ta, Nb, and Zr have been discussed.[24] These elements are notorious for occluding undissolved particles and cohydrolyzing or coabsorbing analytes.[24,105,123,167] Systematic procedures for analyte recovery have been evolved, and the majority involve the elimination of silicon and the use of complexing agents which preclude hydrolysis. The complexing of elements other than silicon is discussed in Sections V.B.1 and V.B.2. When silicon is to be determined, a separate group of procedures is available to retain the analyte completely in solution. These are separately discussed in Sections V.B.1 and V.B.2.

Two general approaches to silicon removal and analyte recovery are discussed in the literature as follows:

1. The sample solution is evaporated to dryness with low boiling point acids (e.g., HNO_3, HCl)[3,30-32,168,169] or to fumes with higher boiling point acids (e.g., H_3PO_4, H_2SO_4, $HClO_4$).[39-41,77] The evaporate is resolved and filtered. The insolubles are ignited at 600°C in a platinum crucible, fumed with hydrofluoric and sulfuric acids to remove silicon, fused with acid (bisulfates)[3,77,167] or alkaline (carbonates and/or borates)[124,168,169] fluxes, and returned to the original filtrate or analyzed separately. Cobb et al.[169] selected alkaline rather than bisulfate fluxes because a clear solution was recovered in the presence of titanium, niobium, and zirconium and sodium salts rather than potassium to achieve less erosion of platinum ware.

2. Alternatively, hydrofluoric acid[3,112,166] may be added as part of the dissolution technique in a PTFE beaker, followed by evaporation to dryness or fumes, and recovery with the desired media. This technique has the following advantages: usually avoiding filtration, confining the dissolution to one vessel, no added fluxes, and of no erosion contamination from platinum vessels. The limitations are the necessity to use plastic ware entirely for dissolution and storage, a failure to dissolve several phases insoluble in hydrofluoric acid, and difficulty in removing residual traces of hydrofluoric acid.

Insoluble residues vary considerably with each differing iron ore, varying alloy composition, or prior metallurgical history. Failure to resolve insoluble residue represents one of the most serious aspects of varying bias and accuracy difficulties in ferrous analyses. Despite the overwhelming evidence that partly or fully dehydrated silica retains analytes or that insoluble residues should be fully dissolved, a number of workers justify recommendations that these not be included with the prepared solution; alternatively, many workers ignore the residues. Thus, Nakahara et al.[127] did not dissolve the insoluble residues when determining silicon in steel. Sellers[170] claims that the loss of lead was less than 1 μg/g when determining 4 to 136 μg/g lead in steel. Fassel et al.[12] observed visible insoluble residues, particularly in high carbon and silicon steels, and claimed that OES showed these to contain insignificant nondetectable levels of the analytes (Al, Co, Cr, Cu, Mn, Ni, and V), which is certainly inconsistent with reported experiences with aluminum. The reviewer feels that a better choice of standard reference materials and the use of fully matrix-matched calibration standards would have disclosed more serious difficulties. Shaw and Ottaway[158] indicate that the justification of nonfiltration and evaporation is the avoidance of contamination when using an electrothermal furnace technique.

The reviewer suggests the use of rigorous dissolution techniques on all occasions when precise and accurate analyses are required to establish a procedure or to provide a calibration value for a proposed reference material. With this basic approach, no objection can then be made to the shortening of quality control analysis procedures when a routine and fully characterized material is being produced or processed.

There are a number of differences in approach between the solution preparation of alloys and oxides, and, accordingly, the ensuing subsections are divided. The solution preparations range from 10% (mass/vol) for trace elements[53] to the more conventional 2 to 0.5% (mass/vol) down to 0.01% (mass/vol) for major analyte concentrations.[110,118] A notable feature of the development of electrothermal GF methods is a trend towards the use of only one acid in the solution medium, so that uniform predictable reactions can be achieved in the drying, ashing, and atomization stages.

1. Alloys

The majority of simple or complex alloys are soluble in separate or combined mineral acids. With due regard to the dissolution properties of a particular alloy, acid combinations are chosen to be most advantageous to the ensuing determination of the analytes by atomic spectrometry. A brief outline of the advantages and limitations of a number of dissolution techniques is proposed, with only limited reference to suitability for specific analytes. The actual acid media for any determination are given in Section VI, where some illustrative details are indicated for each element. The descriptive title for each acid medium tends to reflect the final determinative media without particular regard to the initial dissolution.

a. Hydrochloric Acid Medium

Hydrochloric acid medium provides rapid dissolution, and, in many instances, has been used without evaporation prior to determination.[42] If evaporation is carried out, hydrofluoric acid can be used to volatilize silicon[68,69] and nitric acid used to achieve oxidation of carbides and iron (II). Nitric acid is also beneficial in assisting the dissolution of alloys which are resistant to hydrochloric acid alone.[45,101,104,130,168,170] When nitric acid cannot be tolerated, hydrogen peroxide or ammonium persulfate can provide substantial oxidative capability. Alternatively, formic acid can destroy residual nitric acid following an evaporation to dryness.[55,56] Hydrochloric acid, when used in the absence of an oxidizing media, can on occasion suffer volatility losses of As, P, Se, Sb, and Te.[24]

The anodic dissolution of a 15-mg sample from a cast iron pin in 30 sec (using 20 ml of 2 *M* hydrochloric acid) is effective.[16] A power supply delivers a constant current of 2 A at 150 V DC to a plastic electrolysis cell with a graphite rod cathode. The advantages of anodic dissolution for the AAS determination of magnesium are the ability to analyze liquid hot metal in 1.5 min, the low anion concentration of the electrolytic dissolution media, and no sample weighing is required. Some difficulties such as a 91% efficiency with a relative standard deviation of 4% were experienced (when compared with Faraday's law), some sample surface preparation was required, the solvent choice had a critical bearing on uniform dissolution, and a limitation to the determination of minor constituents. A further difficulty was a 0.011% negative bias at 0.09% magnesium. The reviewer believes this was due to the nonsolution of magnesium oxide inclusions falling to the base of the electrolysis cell.[52] Clearly, the technique has some advantages for dedicated on-line control, particularly for analytes which do not form carbides and inclusions in the solidified alloy.

b. Hydrochloric + Nitric Acid Media

Hydrochloric + nitric acid mixtures (e.g., aqua regia) can be beneficial to speed the solution rate of samples and will achieve the dissolution of most ferrous alloys. In many instances, this media has been used for determinations without a preceding evaporation.[53,58,113,119,122,171] A 15% (v/v) hydrochloric + 5% (v/v) nitric acid solution will dissolve steel for silicon determinations[24,119,172] without analyte hydrolysis.

c. Nitric Acid Medium

Nitric acid develops passivity with a number of ferrous alloys, often giving poor cleanup of insoluble residues. Alternatively, the initial preparation may be achieved with hydrochloric + nitric + hydrofluoric acids, and, following a low-temperature evaporation, recovery is achieved in nitric acid. This medium is particularly suitable for electrothermal furnace applications.[8,82]

d. Hydrochloric + Hydrofluoric + Nitric Acid Media

This acid mixture was specifically designed for the determination of silicon and requires exclusive preparation and storage in PTFE.[66,129] Alternatively, the initial dissolution of the sample may be achieved by hydrochloric + nitric acid, with subsequent resolution of the partly dehydrated silica by hydrofluoric acid.[173] Although this acid media is suitable for retaining otherwise hydrolyzable analytes in solution, due regard must be given to the potential interference of orthosilicate anion.[117,118,124,125] Application to seven elements in complex alloys has been proposed.[37,106,135]

e. Phosphoric + Sulfuric Acid Media

This acid media has the general advantage of dissolving carbides, dehydrating silica, and retaining Mo, Nb, Ta, Ti, W, and Zr in solution without hydrolysis. For some alloys, dissolution can be assisted by the use of aqua regia. Insoluble residues may be removed by filtration and resolved.[24,92,126]

f. Perchloric Acid Medium

Perchloric acid, an ideal medium for many atomic spectrometric analyses, is an efficient dehydrating agent for silicon and a powerful oxidant for carbides. Accordingly, silicon may be simultaneously determined by the gravimetric method[174] and absorbed analytes recovered. Major amounts of chromium may be removed as chromyl chloride (CrO_2Cl_2) by making careful dropwise additions of hydrochloric acid while perchloric acid is fuming.[175,176]

Three supporting variants are[10,22,58,64,67,127] the use of hydrofluoric acid during dissolution to achieve volatilization of silicon, the use of hydrofluoric acid in the cold and after fuming to solubilize silica prior to a silicon determination, and the simultaneous use of phosphoric-sulfuric acid to retain tungsten and molybdenum in solution for determination.

g. Sulfuric Acid Medium

This medium exhibits a very slow dissolution rate for many ferrous alloys, but three uses are noted: Schiller[177] dissolves 60-g samples of steel in 600 ml of 3 *N* sulfuric acid and recovers insoluble niobium carbide by filtration; however, the method failed to recover all niobium when a 16% Cr-steel with a very low carbon content was examined. A sulfuric acid medium was found advantageous for GFAAS, and insolubles were redissolved by fusion with sodium bisulfate;[77,96] and 2 to 3 *N* sulfuric acid was used to dissolve steel for the determination of silicon.[126,128,172]

2. Oxides

The majority of oxides encountered in ferrous metallurgical analysis could be classed as natural or processed iron ores. Where solution is attempted solely with mineral acids, iron ores are usually characterized by a residual presence of clays and spinels, which may be resistant even to hydrofluoric acid. While complete resolution can usually be obtained with a direct fusion[125,129] or sinter,[178] there is a general tendency to carry out a preliminary acid dissolution and evaporation prior to fusion; then, silicon can be removed by volatilization, and the salt concentration derived from fluxes may be limited or optimized advantageously for atomic spectrometric determinations. Often, the flux concentration may be optimized to achieve a subsequent ionization control function.

The ASTM has developed a comprehensive sample preparation method for iron ore, which can be used as a common base media for several analytes.[34,35] The ideal concentration ranges for each analyte, and the ionization control or enhancing agent concentrations are achieved through subsequent dilutions and additions. This approach encourages a comprehensive and complete method of sample dissolution, justified by the subsequent number of determinations which can be achieved. The disadvantage is the extensive number of subsequent dilutions.

The ASTM procedure digests the -75-μm sample particles with hydrochloric acid, followed by nitric acid, and evaporates to dryness. Following digestion with hydrochloric acid and water, the sample is filtered. The paper and residue are ignited in a platinum crucible and then heated with sulfuric + hydrofluoric acids to volatilize most silica. Following fusion with sodium carbonate, the extract is returned to the main filtrate.[34,35] Similar procedures are proposed,[3,28,39–41,48,124,168] with the main variants being the use of mixed borate + carbonate or alkali bisulfate fluxes. The mixed borate + carbonate fluxes are preferred because of ease of dissolution of flux after cooling. The preparations are also suitable for determinations of Al, Bi, Ca, Cr, Co, Cu, Pb, Mg, Mn, Ni, Ti, V, and Zn. The SAA procedures offer several distinct advantages over the above methods:[39,41] perchloric acid is used to dehydrate silica for easier filtration; an addition of 0.2 ml sulfuric acid (sp. gr. 1.84) complexes titanium in solution and successfully avoids the hydrolysis problems discussed and inadequately dealt with by ASTM; and the fusion is extracted within the crucible with a magnetic stirring bar, and, hence, the extract is added to the reserved filtrate instead of the dubious practice[34,35] of immersing the fusion crucible in the reserved filtrate where any acquired exterior surface contamination is added to the assay.

A common preparation for the determination of sodium and potassium in iron ore involves sample dissolution in hydrofluoric hydrochloric acid and evaporation to dryness[115,166] or, alternatively, to fumes with perchloric acid.[3,28] This preparation may also be used for the determination of all analytes discussed in the preceding paragraph. The reviewer expresses the following preferences: (1) perchloric acid evaporation be used, (2) the residue be recovered by filtration,[112] and (3) the mutual enhancement of alkali elements be avoided by using a nonanalyte alkali for ionization control (e.g., Li or Cs). Perchloric acid achieves a more certain removal of hydrofluoric acid, thereby avoiding the retention of insoluble fluorides (e.g., CaF_2). The insoluble residues are significant and often contain alkali elements in clays and spinels. It is usually convenient to resolve the insoluble residues with a flux containing the desired ionization control agent, or, alternatively, the resolved residues may be treated as a separate assay.

Samples of −150-μm particles were dissolved by pressure solution in thick-walled polypropylene bottles using 90% (v/v) hydrochloric + 10% (v/v) hydrofluoric acid at 120°C.[118] After cooling, boric acid was added to dissolve precipitated fluorides, and the preparation was suitable for the determination of a range of elements including silicon. Likewise, a PTFE vessel was used in an autoclave with continuous magnetic stirring at 150°C.[117] The advantage over the above-mentioned method is the retention of silicon when required, and while pressure increases the solubility of spinels and clays, the reviewer is not satisfied that complete solution would always be achieved and recommends the recovery and fusion of any insoluble residues as discussed above.

C. Concentration and Separation Procedures

To improve c_L values by significant factors, analyte preconcentration procedures represent the most suitable option for removing interfering quantities of iron from the solution media and eliminating undesirable anions or cations derived either from the constituents of the sample or dissolution procedures. In the past decade, atomic spectrometry has provided a stimulus to the development of improved separation and concentration procedures in order to reach the c_L required by the ferrous metallurgical industry. This stimulus has recently fallen into abeyance because the c_L required by the industry can be more readily reached by the use of electrothermal furnace techniques without preliminary separation as discussed in Section IV.C.3. However, as further consolidation studies are made and suitable standard reference materials become available, the reviewer suggests that preconcentration and separation procedures will acquire a new importance. It is convenient to arrange discussion into three ensuing subsections on solvent extraction of iron, solvent extraction of analytes, and miscellaneous separations.

1. Solvent Extraction of Iron

The solvent extraction of chloroferrate species from hydrochloric acid media was reviewed by Belcher.[24] Recent work has used only one extraction with the solvent to remove iron (III) prior to the determination of aluminum,[14,167,169] calcium,[179] lead,[176,180,181] and cobalt, copper, nickel, and zinc.[3]

A 5% (mass/vol) iron solution in 90 ml 9 *M* hydrochloric acid medium can be reduced to 0.15% (mass/vol) iron by a single extraction with 150 ml isobutyl acetate.[14,167,169] The studies show that for maximum efficiency, the hydrochloric acid concentration should not be allowed to fall below 8 *M*, so that a reproducible residual iron concentration can be maintained for each assay.

Methyl isobutyl ketone (MIBK) is a similarly effective solvent, but recent examples used relatively lower iron concentrations and acidities requiring two solvent extractions and giving overall lower extraction efficiencies and unnecessarily increasing blank rates and losses.[3,176,181] Hofton and Hubbard[180] used isopropyl ether, a hazardous and less efficient solvent.

The reviewer feels that several aspects of the technique require care when preparing solutions for solvent extraction of chloroferrate species: a PTFE beaker is useful for lowering blank rates; acid and solvent should be selected for low blank rates; the initial solution of the sample in hydrochloric acid should be evaporated to dryness to dehydrate silicon, so that the insoluble matter can be filtered more easily; hydrochloric acid of the chosen molarity for extraction should be used to resolve the evaporate, to wash the beaker and insoluble residues, and to resolve the insoluble residues after fusion; and the residual anions and/or cations from the flux may be optimized to serve also as enhancement or ionization control agents.

2. *Solvent Extraction of Analytes*

Significant contributions to the solvent extraction separation of analytes in the range 0.1 to 100 μg/g (using sample weights as heavy as 10 g) have been made by using iodide/MIBK for bismuth[68,69] or antimony,[182] thiocyanate/MIBK for tin,[183] and iodide/trioctylphosphine oxide (TOPO)/MIBK for antimony, bismuth, lead, silver, thallium, and tin.[55,56,59,60] All these methods use extraction from 0.5 to 2.5 *M* hydrochloric acid in the presence of ascorbic acid as reductant and potassium iodide, so as to form iodides with the analytes. TOPO is used in combination with iodide in order to tolerate wider variations in reactants, enabling the simultaneous quantitative extraction of several analytes. The c_L values are as low as 0.1 μg/g, and the relative standard deviations range from 3 to 10% at the 100 to 5 μg/g levels. The main difficulties are that copper and, to a lesser extent, antimony, bismuth, and tin are the main interfering elements, but, in practice, up to 50 mg can be controlled by increasing the iodide concentration; the MIBK extracts water, hydrochloric acid, and inorganic salts, which can cause nonspecific absorption; while silver (I) and thallium (I) can form insoluble chlorides, they are sufficiently soluble with the acidity and analyte concentrations used, provided another chloride insoluble matrix element is not present. Also, a significant number of other minor and trace elements are extracted and can be tolerated by AAS, but would cause increased difficulties for AES and AFS.

Ichinose[184] developed a solvent extraction AAS procedure for 0.002 to 1 mg/g copper using zinc dibenzyldithiocarbamate extraction with MIBK from 0.75 *M* sulfuric acid. Kisfaludi used the well-proven dithizone in carbon tetrachloride extraction procedure at pH 9.2 in the presence of potassium cyanide and citric acid to determine 1 to 25 μg/g lead[185] and bismuth.[186] The indirect determination of phosphorus by the AAS determination of molybdenum (after specific extraction with isobutylacetate of phospho-12-molybdic acid formed in 1.5 *M* perchloric[160] or 1.2 *M* nitric[161] acids) was used for the determination of 0.01 to 0.15% phosphorus in ferrous alloys.

The most obvious development in the period is the increasing iron media sample mass, prepared and complexed prior to stripping trace concentrations of analytes. For the quoted examples of thallium[55] and silver,[56] the ratio of sample mass to c_L is 10^7:1. The analytes reviewed in this subsection have been analyzed using conventional flame AAS; however, if electrothermal furnace techniques had been applied, c_L values of 1 ng/g would appear to be forthcoming. Obviously, continued development will provide further serious competition for the well-established spark source mass spectrometric technique.

3. *Miscellaneous Separations*

The mercury cathode separation is well established for sulfuric or perchloric acid media, with the advantage over solvent extraction of the chloroferrate species that nickel and chromium are removed with iron.[24] Present-day usage is limited; however, an extensive study was made of the removal of Cr, Fe, Mn, and Ni, present in hydrochloric acid medium.[116] The advantages of hydrochloric acid medium were that no analytes were added with reagents and that hydrochloric acid was the only acid medium suitable for subsequent determination of the alkali and alkaline earth elements in stainless steel by AES. Some increased difficulties with hydrochloric, as compared with sulfuric or perchloric acid media, should be noted: chlorine is generated, a platinum-iridium electrode is required to avoid chlorine attack, a minimum concentration of 0.8 *M* hydrochloric acid is required to avoid deposition of a black film of manganese on vessels and electrodes, and a maximum concentration of 2.0 *M* hydrochloric acid is required to avoid oxidation of chromium (III → VI).

Vasillaros proposed manganese dioxide precipitation and collection of 0 to 200 μg/g lead and bismuth in iron and superalloys. Chromium must be oxidized to chromium (VI) in order to avoid reaction between manganese (VII) and chromium (III), and a 50:1 concentration factor can be achieved.[57]

Sellers[172] and ASTM[30-32] have demonstrated the applicability of an alkyl quaternary ammonium, anion-exchange resin in chloride form (8% cross-linkage), to separate lead from chromium, iron, and nickel in complex steels in 1 *M* hydrochloric acid. The lead is eluted with 12 *M* hydrochloric acid, but variable recoveries of the order of 95% tend to introduce an unnecessary bias to the procedure.

Headridge and Sowerbutts[131] used Zeo-Karb® 225 ion-exchange resin to separate vanadium from a 0.75 *M* hydrochloric acid solution saturated with chlorine water. Vanadium is removed from the column with 1.8 *M* hydrochloric acid saturated with chlorine water, then with 4.5 *M* hydrochloric acid, with both eluates being collected. Two experimental details of note are that chlorine is used to maintain the species vanadium (V) and that chlorine was used to maintain oxidizing conditions because hydrogen peroxide caused bubbles in the ion-exchange column. Vanadium is subject to significant enhancement and depression in AAS; hence, a separation and concentration are justified.

The main advantage of the foregoing separation procedures is a demonstrated ability to allow the beneficial separation of major matrix alloying elements (together with iron) from the analyte. The limitations of the procedures are tediousness and low recovery of analytes.

VI. DETERMINATION OF SPECIFIC ELEMENTS BY SOLUTION TECHNIQUES

The literature examined for this review covered direct determinations of 32 elements and the indirect determination of phosphorus. Accordingly, it is desirable to contrast solution procedures and illustrate significant experimental conditions for each element. The limited applications of direct sampling and analysis of solids procedures were discussed in Section IV.B. No attempt is made to tabulate all methods, as these are adequately covered by annual publications such as *Annual Reports on Analytical Atomic Spectroscopy* and *Analytical Chemistry – Annual Reviews.*

A deficiency of literature on atomic spectrometry lies in the failure to list typical residual, minor, and major alloying levels for each element in iron and steel and provide an indication of the effect on physical properties; furthermore, specification data on iron ores are seldom discussed. These data are important for method design or development, and, accordingly, where possible, brief outlines are given.

For each element, the discussion is subdivided into flame and nonflame groupings. Hydride evolution methods are listed under the nonflame grouping. For the sake of brevity, details are provided in semitabular form, with the aim of providing a starting point for future research workers or less frequent users of ferrous materials.

A. Aluminum

Aluminum is a residual (2 to 50 μg/g), deoxidation (50 to 200 μg/g), or alloying (0.05 to 15%) element in alloys.[24] When Al is used as an oxygen scavenger, the presence of acid-soluble Al indicates that sufficient Al has been added.[153] The insoluble forms occur as nitride, corundum, α-Al_2O_3, and slag and should be dissolved.[123] Iron ore specifications limit Al to < 2% and require Si/Al ratios > 1.5.[18]

1. Flame

AAS methods for alloys use 1 to 2% (mass/vol) Fe in 10% (v/v) HNO_3,[187] 10% (v/v) $HClO_4$,[10] 10% (v/v) HCl + 10% (v/v) HNO_3,[119] 7.5% (v/v) HCl + 2.5% (v/v) HNO_3,[172] or 20% (v/v) HCl[168] with 2 mg/ml Na[168] or 0.4 to 3 mg/ml K[172,187] for ionization control to achieve a c_L of 50 μg/g.[3,20] Using AAS pulse nebulization with 4 or 10% (mass/vol) Fe in 40% (v/v) HCl,[98] 35% (v/v) HCl + 15% (v/v) HNO_3,[53] c_L values of 2 or 7 μg/g were achieved with a S_r of 3% at a level of 12 μg/g.[53] Following solvent extraction of chloroferrate species with concentration to 20% (mass/vol) in 50% (v/v) HCl, AAS methods use 6 mg/ml K[14,167] or 5 mg/ml Na[169] for ionization control; a c_L of 0.2 μg/g[14] was achieved for the concentration range 2 to 100 μg/g, and a S_r of 10% was attained at the 3.6 μg/g level.[14] The upper concentrations of ionization control elements are unnecessarily high.

AAS methods for iron ore mainly involve acid dissolution followed by fusion of insolubles to give 0.15 to 0.6% (mass/vol) Fe in 2 to 20% (v/v) HCl[3,34,48,124,168] or 6% (v/v) $HClO_4$ + 7% (v/v) HCl[39] with 1 to 7 mg/ml Na[34,39,48,124,125,168] or 0.3 to 10 mg/ml K[3,117,188] for ionization control. A c_L of 0.01% with S_r values[39,125] of 1 and 2% can be achieved at the sample concentration levels of 5 and 0.5%, respectively. Normally, 1 to 2 mg/ml La[124,125] is added to overcome Si suppression. Several analysts[117,118,188] prefer sample dissolution with HF in polypropylene bottles (120°C) or PTFE autoclaves (150°C) to yield 0.15 to 0.25% (mass/vol) Fe and use H_3BO_3 to complex F prior to analysis. Again, the upper concentrations used for ionization control are unnecessarily high.

AAS measurements at 309.3 nm use reducing N_2O-C_2H_2; however, some workers prefer the less sensitive 396.2 nm Al line.

For low alloys, AES methods use 0.5 to 1% (mass/vol) Fe in 5% (v/v) HCl[12] or 10% (v/v) $HClO_4$,[22] with 1 mg/ml K[22] for ionization control. For the concentration range 5 to 3000 μg/g, c_L values of 5 or 25 μg/g were achieved and S_r values of 10 or 0.1% were attained at the 5 or 400 μg/g levels, respectively.[13,22] Measurements are made at 396.2-nm line using the N_2O-C_2H_2 flame in slot burners, and background and overlapping band corrections are required.

2. *Nonflame*

GFAAS methods for soluble, insoluble, or total Al in low alloys use 10- to 50-μl aliquots containing 250 to 500 μg Fe, and either 4500 μg H_2SO_4,[77] 2500 μg HNO_3,[153] or 400 μg HCl;[189] and 50 to 70 μg Na when insoluble residues are fused; followed by drying at 95 to 100°C (40 to 50 sec); ashing at 360 to 1660°C (30 to 90 sec); and atomizing at 2400 to 2600°C (10 to 20 sec). Using 309.3 nm, a c_L of 0.5 μg/g[77] can be achieved for the concentration range 2 to 400 μg/g, and S_r values of 6 and 9% can be attained at the 100[153,189] and 10 μg/g levels, respectively. The authors have made conflicting statements regarding the efficacy of various acid media.

B. Antimony

Antimony is deleterious in alloys, being derived mainly from nonferrous components of scrap.[24] Steel, containing > 20 μg/g Sb, cannot be cold rolled[151] and is liable to cracking in welded-steel sections.[156] Usual concentrations of antimony are 0.5 to 300 μg/g in steel[151] and < 10 μg/g in iron ore.

1. *Flame*

AAS methods for alloys use 1% (mass/vol) Fe in 10% (v/v) HCl[74] or 15% (v/v) HCl + 5% (v/v) HNO_3,[3] and, for 50 to 500 μg/g,[3] a c_L of 20 μg/g[74] was achieved. Following solvent extraction, of 1- to 10-g samples from 1.2 to 1.5 *M* HCl/0.2 to 0.3 *M* KI media, using MIBK[182] or 5% (mass/vol) TOPO/MIBK,[59,60] a c_L of 0.1 μg/g was achieved[59,60] for 0.1 to 300 μg/g and S_r values of 3 to 4% can be attained for the 50 to 200 μg/g level.[182] Copper interferes by precipitation and absorption of analyte, but increased KI can suppress this interference.[59] Measurements are made at 217.6 nm using air-C_2H_2, and background corrections are required.[74,91]

2. *Nonflame*

GFAAS methods for alloys use 10- to 25-μl aliquots, containing 10 to 250 μg Fe, either 4300 μg H_2SO_4,[77] 1200 μg HNO_3,[82] or 40 μg HCl + 60 μg HNO_3;[151] with drying at 80 to 100°C (30 sec); ashing at 360 to 850°C (30 to 60 sec); and atomizing at 1900 to 2700°C (5 to 8 sec). Using 217.6 nm, c_L values of 0.3 to 1 μg/g[82,153] can be achieved for the concentration range 1 to 100 μg/g, and S_r values of 18 and 3% can be attained at the 2 and 30 μg/g levels,[151] respectively. An addition of Cr(III) to sample solutions was used to plateau a Cr interference.[156] Many matrix element interferences can be avoided by using the maximum heating rate between the ashing and atomizing temperatures,[151] and background correction is advisable.[77,82,151]

For 40 to 400 μg/g in iron ore,[117] a 25-μl aliquot containing 50 μg Fe, 220 μg HCl, 90 μg HNO_3, 1400 μg HF, and 625 μg H_3BO_3 was used; however, this range is nonapplicable to commercial iron ores, and a lower total preparative salt loading would enable a lower c_L. An AAS hydride evolution technique for alloys uses 20 mg Fe in 16% (v/v) H_2SO_4 + 1.5% (v/v) HCl + 0.5% (v/v) HNO_3 + 3% (mass/vol) KI with a generation volume of 15 ml and 0.3 g $NaBH_4$ as reductant. Calibration curves are prepared for the sample concentration ranges 0 to 50 μg/g (c_L 1 μg/g) (217.6 nm) and 2 to 100 μg/g (231.1 nm); a S_r of 10% was achieved for a standard reference sample containing 300 μg/g. The evolved SbH_3 was atomized in air-entrained Ar/H_2, and background measurements were not required. The Fe concentration was maintained constant irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and > 2% Ni interfered.[58]

C. Arsenic

Arsenic is deleterious in alloys (being derived from iron ores and ferro-alloys) and causes cold-brittleness fracture, particularly in welded steel sections.[24,156] Usual concentrations are 1 to 300 μg/g in alloys and < 100 μg/g in iron ores.

1. Flame

An AAS method for alloys used 1% (mass/vol) Fe in 10% (v/v) HCl and obtained a c_L of 60 μg/g with air-C_2H_2.[74] Pulse nebulization used 10% (mass/vol) Fe in 35% (v/v) HCl + 15% (v/v) HNO_3, and achieved a c_L of 20 μg/g with N_2O-C_2H_2.[53] AAS measurements are made at a 193.7-nm line and background correction is required. High-background flame absorption makes nonflame methods more attractive, and future developments will occur in that area.

2. Nonflame

GFAAS methods for alloys used 5 to 20-μl aliquots, containing 12 to 200 μg Fe, 60 to 1200 μg HNO_3, with drying at 125°C (30 sec), ashing at 500°C (30 sec), and atomizing at 2700°C (8 sec). Using 193.7 nm, a c_L of 0.2 μg/g[82] can be achieved for the concentration range 1 to 30 μg/g, and S_r values of 6% can be attained for the 40 to 300 μg/g concentration levels.[156,190] Difficulties were experienced if HCl, H_2SO_4, or $HClO_4$ media were used.[156]

Two AAS hydride evolution techniques for alloys used 5 to 20 mg Fe in 45% (v/v) HCl + 2% (mass/vol) KI + 0.35% (mass/vol) $SnCl_2$[83] or 20% (v/v) HCl + 2% (v/v) $HClO_4$,[58] with generation volumes of 10 or 50 ml and either 0.3 g $NaBH_4$[58] or 5g Zn[83] as reductant. Calibration curves were prepared for the sample concentration ranges 0 to 50 μg/g (c_L = 1 μg/g) (193.7 nm) and 2 to 100 μg/g (197.2 nm); a S_r of 2% was achieved for a standard reference sample containing 300 μg/g.[58] The evolved AsH_3 was atomized in air-entrained Ar/H_2, and background measurements were not required. The Fe concentration was maintained constant irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and Cu interfered at all levels.[58]

D. Barium

Barium is a minor element (< 0.05%) in most iron ores.

1. Flame

An AAS method for 0.25 to 5% Ba in iron ore used 0.14% (mass/vol) Fe in 0.75% (v/v) HCl + 0.25% (v/v) HNO_3 + 5% (v/v) HF + 2.5% (mass/vol) H_3BO_3 at 553.6 nm with N_2O-C_2H_2.[117] Ionization control was not used, and the range was too high for most iron ores.

E. Bismuth

Bismuth is deleterious in alloys, being derived from scrap and iron ores and steel containing > 2 μg/g, may crack during cold-rolling;[17] > 20 μg/g reduces the hot ductility of stainless steel.[68,69] Usual concentrations are 0.01 to 100 μg/g[8] in alloys and < 10 μg/g in iron ores.

1. Flame

AAS methods for alloys used 1 to 2% (mass/vol) Fe in 10% (v/v) HCl[74] or 15% (v/v) HCl + 5% (v/v) HNO_3,[3] and at the 40 to 1000 μg/g level, a c_L of 40 μg/g was achieved. AAS pulse nebulization, with 6% (mass/vol) Fe in 10% (v/v) HNO_3, achieved a S_r of 8% at the 60 μg/g level together with a c_L of 60 μg/g.[8] Following chloroferrate extraction with MIBK and concentration to 8% (mass/vol), the c_L was lowered to 10 μg/g.[3] Solvent extraction was achieved from: 1- to 10-g samples in 1.2 to 2.3 *M* HCl/0.2 to 0.3 *M* KI media using MIBK[68,69] or 5% (mass/vol) TOPO/MIBK;[59,60] citrate-cyanide buffered media at pH 9.2 with 0.025% (mass/vol) dithizone in CCl_4;[159] or alkaline EDTA-citrate buffered media with ammonium pyrrolidine-dithiocarbamate (APDC) and MIBK.[191] Following solvent extraction, a c_L of 0.1 μg/g[59,60] was achieved for the concentration range 0.1 to 1000 μg/g. Vassilaros[57] concentrated 10 to 100 μg/g Bi to the equivalent of

50% (mass/vol) media by precipitation-collection with MnO_2 and achieved a S_r of 4% at the 20 μg/g level. All the separation/concentration methods described were interference free and applicable to high alloys. In iron ore, AAS for 10 to 1000 μg/g Bi used 0.7% (mass/vol) Fe in 10% (v/v) HCl, with 3 mg/ml K, which is derived from fusion of insoluble residues and has no ionization control function.[3]

AAS measurements were mainly made at 223.1 nm, although 222.8 nm was useful for higher concentrations,[191] and air-C_2H_2 was used exclusively. Background absorption measurements were not required for direct determinations,[8] but this conflicts with other workers.

AFS was used following reaction between an alkaline EDTA-citrate buffered solution and APDC and extraction with MIBK.[191] The c_L of 0.1 μg/g represented a sixfold increase in sensitivity compared with AAS. The procedure was interference free and applicable to high alloys. AFS measurements were made at 306.8 nm using $Ar/H_2/O_2$ with a total consumption burner.

2. *Nonflame*

For alloys, GFAAS methods used 2- to 50-μl aliquots, containing 10 to 500-μg Fe, and either 4300 μg H_2SO_4,[77] 3000 μg HNO_3,[8] or 80 μg HCl + 60 μg HNO_3;[17] with drying at 100°C (30 to 40 sec); ashing at 360 to 800 °C; and atomizing at 1400 to 2100°C (5 to 10 sec). Using the 223.1-nm line for the concentration range 0.5 to 40 μg/g, c_L values of 0.04 to 2 μg/g[153] were achieved, and S_r values of 6 and 2% were attained at the 3 and 20 μg/g levels,[8,17] respectively. Background correction was beneficial.[77] Frech analyzed high alloys, but matrix matched Ni and Cr to 5% (absolute), Fe to 1% (absolute), and Mo precisely.[17] An overlap of specific absorption of Bi with background nonspecific absorption was avoided by chemical reaction with ammonia to raise the temperature at which bismuth atomization commenced.[17]

An AAS hydride evolution technique for alloys uses 20 mg Fe in 10% (v/v) H_2SO_4 + 2% (v/v) $HClO_4$, with a generation volume of 10 ml and 0.3 g $NaBH_4$ as reductant. A calibration curve is prepared for the sample concentration range 0 to 50 μg/g (c_L = 1 μg/g) (223.1 nm) and a S_r of 5% was achieved for a standard reference sample containing 20 μg/g. The evolved BiH_3 was atomized in air-entrained Ar/H_2, and background measurements were not required. The Fe concentration was maintained constant, irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and no interferences were detected.[58]

F. Cadmium

Cadmium occurs as a trace (< 10 μg/g) in alloys, being generally derived from scrap solders. Cadmium is < 10 μg/g in iron ore, except where zinc concentration is significant (e.g., pyrites).

1. *Flame*

AAS used 1 to 2% (mass/vol) Fe in 10% (v/v) HCl[74,192] or 10% (v/v) HCl + 10% (v/v) H_3PO_4[192] and achieved a c_L of 0.5 to 2 μg/g for the 1 to 1000 μg/g level in alloys, using 228.8 nm and air-C_2H_2.

G. Calcium

Calcium is a residual oxide (1 to 200 μg/g) in alloys, derived from slag or deoxidation reactions; Ca improves the machinability of alloys.[193,194] Ca occurs naturally as carbonates, clays, and spinels in iron ores or is added to iron ore to form self-fluxing sinter; accordingly, 0.01 to 10% is found in oxide materials.

1. *Flame*

AAS methods for alloys used 1 to 2% (mass/vol) Fe in 8% (v/v) HCl,[195] 5% (v/v) HCl + 5% (v/v) $HClO_4$,[64] 15% (v/v) HCl + 5% (v/v) HNO_3,[3] or 10% (v/v) $HClO_4$,[52] with 1.5 mg/ml Na + 1.5 mg/ml Sr,[52] 1 mg/ml K + 1 mg/ml Sr,[195] or 2 mg/ml KI + 2 mg/ml I_2O_5[64] for ionization and interference control. Insoluble residues were dissolved by fusion.[52,64] For the concentration range 1 to 200 μg/g, a c_L of 1 μg/g was achieved, and S_r values of 20 and 6% were attained at the 5 to 10 and 20 μg/g levels, respectively.[52,64,195]

AAS methods for iron ore and sinter mainly involved acid dissolution followed by fusion of insolubles to give 0.07% (mass/vol) Fe in 1 to 5% (v/v) HCl[3,35] or 6% (v/v) $HClO_4$ + 7% (v/v) HCl,[40] with 300 μg/ml K^3 or 500 to 1200 μg/ml Na[35,40,118] for ionization control. With the preferred calibration range of 0.2 to 5 μg/ml, a c_L value of 0.01 mass% Ca was achieved and S_r values of 4 and 1% were attained at the 0.1 and 5% concentration levels, respectively.[35,40] An addition of 2 to 5.7 mg/ml La was used to overcome Si suppression interferences.[35,40] Several workers preferred resolution with HF in polypropylene bottles (120°) or PTFE autoclaves (150°) to yield 0.005 to 0.16% (mass/vol) Fe and used boric acid to complex F prior to analysis.[117,118,188] The upper concentration levels of La appear unnecessarily high.

AAS measurements at 422.7 nm used N_2O-C_2H_2; the choice of air-C_2H_2 by several workers is not in accord with present practice.[3,28,29,179]

An AES method, concentrated to 5% (mass/vol) with a mercury-cathode separation, used HCl media at pH 4 and 100 μg/ml Sr to avoid suppression interferences when determining 1 to 10 μg/g in stainless steel with the 624-nm band and air-C_2H_2.[116]

H. Chromium

Chromium is a residual (0.001 to 0.3%) or alloy (0.3 to 30%) in ferrous metals. Chromium occurs as a trace (< 0.05%) in iron ore, although some chromite iron ores (0.1 to 3% Cr) are used. Solution preparations should ensure that all Cr intermetallics are dissolved and that Cr is not occluded in hydrolyzed precipitates.[196]

1. Flame

AAS methods for 0.001 to 25%[10,42,43,67,92] used 0.01 to 2% (mass/vol) Fe in 2 to 20% (v/v) HCl,[42,110] 10% (v/v) HCl + 10% (v/v) HNO_3,[119] 3% (v/v) HCl + 10% (v/v) HNO_3 + 3% (v/v) HF,[106] 10% $HClO_4$,[10,67] or 0.75% (v/v) H_3PO_4 + 0.75% (v/v) H_2SO_4,[92] with 2% (mass/vol) NH_4Cl,[119] 0.25 to 0.9% (mass/vol) 8-hydroxyquinoline,[43,47,110] or 1 mg/ml K[106] to avoid interferences. Typically, S_r values of 0.15 to 1 and 1% were attained at the 20[10,11,67] and 0.2%[43] concentration levels, respectively. Solvent extraction of Cr(VI) from 1 to 3 *M* HCl with MIBK was achieved after complexing Fe(III) with fluoride; the method required cold oxidation with Ce(IV) and was tedious.[197]

For 10 to 5000 μg/g in iron ore, AAS used 0.7% (mass/vol) Fe in 10% (v/v) HCl with 3 mg/ml K; the K is derived from the flux and used for ionization control.[3]

AAS measurements were made at 357.9 nm with N_2O-C_2H_2 or air-C_2H_2. As indicated in Section IV.C.1.d.v.c, a lean N_2O-C_2H_2 flame and Cr (III) are preferred.

An AES method for 0 to 1% in alloys used 0.5% (mass/vol) Fe in 5% (v/v) HCl achieving a c_L of 0.002 mass% and a S_r of 1% was attained at the 0.06% level using 357.9 nm with N_2O-C_2H_2; background and overlapping band corrections were required.[12]

An AFS method used 0.02% (mass/vol) Fe in HCl-HNO_3 for 0.5 to 25%, or prior chloroferrate extraction for 0.03 to 0.5%, and achieved a S_r of 2% at the 2% concentration level with 359.4 nm and separated air-C_2H_2.[121] For highest efficiency, the solvent extraction should have been affected from 5 to 10% rather than 0.02% (mass/vol) medium.

2. Nonflame

GFAAS for alloys used a 25-μl aliquot containing 250 μg Fe and 4300 μg H_2SO_4, with ashing at 360°C. For the 0 to 20 μg/g concentration level, a c_L of 0.5 μg/g was achieved at 357.9 nm line. No interferences were encountered, and background correction was beneficial.[76]

For 10 to 100 μg/g in iron ore by GFAAS, a 25-μl aliquot containing 50 μg Fe, 220 μg HCl, 90 μg HNO_3, 1400 μg HF, and 625 μg H_3BO_3 was used at 357.9 nm.[117]

I. Cobalt

Cobalt is a residual (< 0.1%) in alloys and a serious problem in austenitic steel (< 100 μg/g) for the nuclear industry;[105] alloying additions (0.5 to 30%) are used for special steels. Iron ores contain < 50 μg/g, although some nickel-bearing iron ores contain to 500 μg/g.

1. Flame

AAS methods for alloys used 1 to 2.5% (mass/vol) Fe in 10% (v/v) $HClO_4$,[10,103] 15% (v/v) HCl + 5% (v/v) HNO_3,[37] or 20 to 25% (v/v) HCl,[104,105] and for the concentration range 5 to 5000 μg/g, a c_L of 1 to 5 μg/g[103,104] was achieved, and S_r values of 14 and 2% were attained at the 120 and 600 μg/g levels, respectively.[103] A 15% (v/v) HCl + 5% (v/v) HNO_3 + 5% (v/v) HF media was recommended for alloys containing hydrolyzable elements.[37]

For 5 to 1000 μg/g in iron ores or pyrites, AAS methods used 0.7 to 1.4% (mass/vol) Fe in 10 to 22% (v/v) HCl (with 3 mg/ml Na or K derived from fluxes), and a S_r value of 5% was achieved at the 150 μg/g level.[3,124] Serious interference, caused mainly by Fe, Cr, and Ni,[103,105] may be overcome by using oxidizing air-C_2H_2 or preferably N_2O-C_2H_2. Enhancement was encountered from Ti and V unless oxidizing air-C_2H_2 was used.[104]

AAS measurements used 240.7 nm, and N_2O-C_2H_2 is recommended as discussed in Sections IV.C.1.c and IV.C.1.d.v.c.

For the 50 to 5000 μg/g concentration range in low alloys, AES used 0.5% (mass/vol) Fe in 5% (v/v) HCl and achieved a c_L of 50 μg/g, and a S_r of 2% was attained at 1400 μg/g by using 345.4 nm with N_2O-C_2H_2. Background and overlapping band corrections were required.[12]

An AFS method used 2% (mass/vol) Fe in 30% (v/v) HCl + 15% (v/v) HNO_3 for 100 to 200 μg/g in alloys. For lower ranges, a prior chloroferrate extraction would be required, and dilutions were used for higher ranges; a S_r of 4% was achieved at the 1300 μg/g concentration level using 240.7 nm with argon-separated air-C_2H_2, and no interferences are observed.[198]

2. Nonflame

GFAAS for 40 to 400 μg/g in iron ore used 240.7 nm and a 25-μl aliquot, containing 50 μg Fe, 220 μg HCl, 90 μg HNO_3, 1400 μg HF, and 625 μg H_3BO_3, with drying at 100°C (30 sec), ashing at 1150°C (30 sec), and atomizing at 2650°C (15 sec).[117]

J. Copper

Residual Cu (0.001 to 0.3%) is derived mainly from nonferrous scrap and is deleterious for welding or tinplate manufacture; alloying (0.2 to 10%) additions impart special properties.[24] Iron ore specifications limit Cu to $\ngtr$ 200 to 500 μg/g.[18]

1. Flame

AAS methods for alloys used 0.2 to 1% (mass/vol) Fe in 10% (v/v) $HClO_4$,[10] 10% (v/v) HCl + 10% (v/v) HNO_3,[119] 2% (v/v) HCl,[110] or 4.5% (v/v) H_2SO_4 + 4.5% (v/v) H_3PO_4;[199] for the concentration level 0.001 to 3%,[119,199] a S_r of 0.5% was achieved. Solvent extraction from 0.75 *M* H_2SO_4 with 0.05% (mass/vol) zinc dibenzyldithiocarbamate in MIBK was used to determine 2 to 50 μg/g in alloys; no interferences were experienced from 16 diverse elements. A c_L of 1 μg/g was achieved, and S_r values of 5 and 2% were attained at the 1 and 100 μg/g concentration levels, respectively.[184]

For 0.001 to 0.8%,[3,124] AAS methods for iron ores used 0.3 to 1.4% (mass/vol) Fe in 5% (v/v) $HClO_4$[112] or 10 to 22% (v/v) HCl,[3,124] achieving a S_r of 2% at the 0.4% concentration level.[112] The solutions contained 3.3 mg/ml Na[124] or 3.0 mg/ml K[3] derived from fluxes, which, however, were not required for ionization control.

AAS measurements used 324.7 nm with air-C_2H_2, and background corrections were recommended for the lower ranges.[112]

For 0.01 to 0.2% in low alloys, AES used 0.5% (mass/vol) Fe in 5% (v/v) HCl, achieving a c_L of 0.01 mass% and a S_r of 1% at the 0.08% concentration level; measurements at 324.7 nm used N_2O-C_2H_2. Background and overlapping band corrections were required.[12]

K. Gallium

Gallium is residual (2 to 80 μg/g) in steel, affecting the hardness of Fe-Ni alloys.[96]

1. Flame

AAS methods for alloys used 4% (mass/vol) Fe in 30% (v/v) HCl with either air-C_2H_2 or N_2O-C_2H_2, achieving a S_r of 17% at the 20 μg/g concentration level with the 294.4 nm line. Fe interference was serious at the more sensitive 287.4 nm wavelength.[96]

2. Nonflame

GFAAS for alloys used a 50-μl aliquot, containing 500 μg Fe and 17 mg H_2SO_4, with drying at 100°C (60 sec), ashing at 1100°C (60 sec), and atomizing at 2600°C (30 sec). A S_r of 3% was attained at the 20 μg/g concentration level using 294.4 nm, and no interferences were experienced from 25 mass% Cr or Ni.[96] Clearly, the method is more suitable than the conventional flame technique.

L. Iron

The necessity to match the iron concentration of assays and calibration series was discussed in Sections III.D and IV.C.1.d.i. This may require an analysis for 50 to 100% Fe, preferably using the same solutions prepared for other analytes.

1. Flame

AAS methods for Fe in alloys used 0.5 to 2.0% (mass/vol) Fe in 15% (v/v) HCl or 4.5% (v/v) H_2SO_4 + 4.5% (v/v) H_3PO_4 and a S_r of 0.7% was attained at the 100% concentration level using oxidizing air-C_2H_2. Similar results could be expected with alternative acids and Fe concentrations. The use of wavelengths with much higher than usual c_L values was favored by a desire to determine Fe without dilution. Approximately 42 wavelength lines, many of which did not have a lower energy level commencing in the ground state, were examined. Hence, 376.7 nm was recommended for 1 to 2% (mass/vol) Fe in HCl and 392.0 nm for 0.5 to 1% (mass/vol) Fe in H_3PO_4 + H_2SO_4 or 0.5% (mass/vol) Fe in HCl. Minor depressive interferences were experienced from Cr, Ni, and W.[45]

For 40 to 70% Fe in iron ore, AAS used 0.02 to 0.12% (mass/vol) Fe in HCl + HNO_3 + HF + H_3BO_3, and a S_r of 2% at the 60% Fe concentration level was attained using 248.3 nm and air-C_2H_2.[117,118]

M. Lanthanum

Lanthanum improves the ductility and impact strength of heat-treated carbon steels and aids successful deoxidation and desulfurization of special steels; a typical residual level is 1 to 50 μg/g.

1. Flame

An AES method for 10 to 80 μg/g in steel concentrated to 10% (mass/vol) following mercury cathode separation and MIBK extraction with 2-thenoyltrifluoroacetone. The band spectra of La at 743 nm was used with air-C_2H_2 in a meker burner.[200] The proposed method is tedious and complicated and would not be competitive even with OES or XRFS techniques which use dissolution preparative methods.[201,202]

N. Lead

Specifications of < 20 μg/g are typical because Pb induces "Widmanstatten" structure, which can cause catastrophic failure in cast irons or hot rupture during the rolling and forging of stainless steel.[158] The machinability of steel is improved with 0.1 to 0.5%. Pb (10 to 50 μg/g) derived from iron oxide is deleterious in the iron blast furnace;[18] pyritic cinders may contain upwards of 2 mg/g.[124]

1. Flame

AAS methods for alloys used 1 to 2% (mass/vol) Fe in 10% (v/v) $HClO_4$[3,10] or 10% (v/v) HCl;[74] for 30 to 3000 μg/g, a c_L of 10μg/g[10,74] was achieved, and background measurements were beneficial.[74] Chloroferrate extraction of stainless steels, with $HClO_4$ fuming and removal of CrO_2Cl_2, was used to give 4% (mass/vol) (5 to 25 μg/g) or 2% (mass/vol) (20 to 100 μg/g) in 40% (v/v) $HClO_4$ + 12% (v/v) HCl for S_r values of 8 and 4% at the 20 and 125 μg/g concentration levels, respectively. Mo and Ni did not interfere.[176] Solvent extraction is achieved from: 1- to 10-g samples in 0.6 to 1.2 *M* HCl/0.15 to 0.3 *M* KI media using MIBK[180] or 5% (mass/vol) TOPO/MIBK,[59,60] or citrate-cyanide buffered media at pH 9.2 with 0.025% (mass/vol) dithizone in CCl_4.[185] Following solvent extraction, a c_L of 0.1 μg/g was achieved for the 0.1 to 1000 μg/g concentration range, and the methods were interference free.[59,60] Ion exchange onto "Dowex®" 1-X8 (Cl-form) from 1 *M* HCl was used to separate Pb from high-alloy matrices, and elution to 50% (mass/vol) was achieved with 12 *M* HCl. The recommended calibration range was 2 to 30 μg/ml. A c_L of 2 μg/g was achieved for the 4 to 5000 μg/g concentration range, and S_r values of 8 and 22% were attained for the 12 to 30 and 1000 μg/g levels, respectively. Recoveries were approximately 95% at 40 μg/g.[30-32,170] However, better precision and accuracy could be obtained with direct determinations using background measurements or solvent extraction procedures. Vassilaros[57] concentrated 10 to 200 μg/g to 50% (mass/vol) by precipitation collection with MnO_2, achieving a S_r of 4% at the 20 μg/g concentration level.

AAS methods for iron oxides used 0.7 to 3.4% (mass/vol) Fe in 8 to 22% (v/v) HCl.[3,28,29,109,124] For 1 to 1000 μg/g, S_r values of 3 and 2% were attained at the 30 and 2000 μg/g levels, respectively. Also, 3 mg/ml Na[124] or K[3] derived from fusion fluxes was not required for ionization control. Matsumoto et al.[181] concentrated to 7% (mass/vol) in 20% (v/v) HCl by using a chloroferrate extraction for 10 to 100 μg/g and achieved a S_r of 2% at the 50 μg/g concentration level. Also, solvent extraction, with 0.1% (mass/vol) dithizone in MIBK from a buffered citrate-triethanolamine media at pH 9.8, was used for 1 to 100 μg/g, and a S_r of 2% at the 50 μg/g concentration level was achieved.[181]

AAS used air-C_2H_2 and mainly 217.0 nm, although a significant number of workers chose 283.3 nm. Background measurements were mandatory unless the analyte was solvent extracted with a specific chelating agent.[74,91,109]

2. Nonflame

GFAAS for alloys used 2- to 20-µl aliquots[82,148] containing 10 to 200 µg Fe in 30 µg HNO_3/20 to 50 µg HCl[148,171] or 1200 µg HNO_3,[82] with drying at 70 to 125 °C (15 to 40 sec) ashing at 490 to 670°C (30 to 50 sec), atomizing at 1150 to 2500°C (5 to 8 sec), and 2800°C for final cleanup. For the sample concentration 1 to 150 µg/g, a c_L of 0.08 to 1 µg/g was achieved, with S_r values of 3 to 10% for standard reference materials containing 30 µg/g Pb, when using 283.3 nm.[153,158]

For 20 to 200 µg/g in iron ore by GFAAS, a 25 µl aliquot containing 50 µg Fe, 220 µg HCl, 90 µg HNO_3, 1400 µg HF, and 625 µg H_3BO_3 was used at 283.3 nm.[117]

An AAS hydride evolution technique for alloys uses 20 mg Fe in 3.8% (mass/vol) tartaric acid + 2.2% (mass/vol) $K_2Cr_2O_7$ + 2% (v/v) $HClO_4$ with a generation volume of 10 ml and 0.3 g $NaBH_4$ as reductant. A calibration curve is prepared for the concentration range 0 to 1000 µg/g (c_L = 7 µg/g) at 217.0 nm, and a S_r of 2% was achieved for a standard reference sample containing 500 µg/g. The evolved PbH_4 was atomized in air-entrained Ar-H_2, and background measurements were not required. The Fe concentration was maintained constant, irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and serious interferences were experienced from Ni and Cu.[58] Fundamental studies of plumbane generation are required.

O. Lithium

Lithium is an ultratrace residual in alloys (0.01 to 5 µg/g) and is < 50 µg/g in iron ores.

1. Flame

An AES method concentrated to 5% (mass/vol) media with a mercury-cathode separation and used HCl at pH 4 (with 100 µg/ml Sr to avoid suppression interferences) when determining 0.1 to 2 µg/g in stainless steel with 670.8 nm and air-C_2H_2.[116]

P. Magnesium

Magnesium is residual (1 to 100 µg/g) or alloying (200 to 2000 µg/g) in ferrous metals or used for desulfurization.[203] Mg occurs naturally as carbonates, clays, and spinels in iron ores and is added to sinters to improve slag fluidity in the iron blast furnace; accordingly, 0.01 to 3% is found in oxide materials.

1. Flame

AAS methods for alloys used 0.075 to 1% (mass/vol) Fe in 2 to 20% (v/v) HCl[16,33] or 10% (v/v) $HClO_4$,[52] with 0.1 to 6 mg/ml Sr to control NH_4(I), Al(III), SiO_3(II), SO_4(II), and PO_4(III) interferences in air-C_2H_2[3,33,113] or 1.5 mg/ml Sr + 1.5 mg/ml Na for ionization and interference control in N_2O-C_2H_2.[52] The upper level of Sr was unnecessarily high. A novel method of anodic dissolution was used to achieve an analysis in 1.5 min.[16] The insoluble residues should be recovered by fusion.[52] For the 1 to 1000 µg/g concentration range, a c_L of 1 µg/g was achieved, and S_r values of 15, 8, and 3% were attained for the 10, 50, and 800 µg/g levels, respectively.[33,52]

AAS methods for iron ore and sinter mainly required acid resolution followed by fusion of insoluble residues to give 0.006 to 0.12% (mass/vol) Fe[40,118] in 1 to 5% (v/v) HCl,[3,35] or 6% (v/v) $HClO_4$ + 7% (v/v) HCl[40] with 1500 µg/ml Sr,[117] 300 µg/ml K + 2000 µg/ml Sr,[3,28] or 1200 µg/ml Na + 5700 µg/ml La[35] to control interference in air-C_2H_2, or alternatively, 500 µg/ml Na[118] or 1200 µg/ml Na + 2000 µg/ml La[40] for ionization and interference control in N_2O-C_2H_2. The upper level of La was unnecessarily high. With the preferred calibration range (0.2 to 3 µg/ml), S_r values of 1 and 4% were attained at the 2 and 0.1% concentration levels, respectively.[35,40] Several workers preferred sample resolution with HF in polypropylene bottles (120°C) or PTFE autoclaves (150°C) to yield 0.005 to 0.16% (mass/vol) Fe and used H_3BO_3 to complex F prior to analysis.[117,118]

AAS measurements at 285.2 nm used either air-C_2H_2 or N_2O-C_2H_2.

2. Nonflame

Preliminary GFAAS indicated a c_L of 0.2 µg/g for alloys.[153]

Q. Manganese

Manganese is a major alloy (0.2 to 14%) in ferrous metallurgy, and, occasionally, 0.001 to 0.2% is required for special materials. Iron ores generally contain < 0.5%, although concentrations to 5% are not uncommon.

1. Flame

AAS methods for 0.01 to 15%[92,119] in alloys used 0.1 to 1% (mass/vol) Fe in 2 to 10% (v/v) HCl,[3,105,110] 1.5 to 10% (v/v) HCl/0.5 to 10% (v/v) HNO_3,[12,119] 10% (v/v) $HClO_4$,[10] 0.75% (v/v) H_3PO_4 + 0.75% (v/v) H_2SO_4,[92] or 10% (v/v) HNO_3 + 3% (v/v) HF + 3% (v/v) HCl[106] and achieved S_r values of 0.3 to 0.6%. The HF or H_3PO_4 media retain hydrolyzable elements in solution, and matrix-matching of the major alloys is required to avoid interferences.

AAS methods for 0.01 to 10% in iron ore used 0.06 to 0.2% (mass/vol) Fe in 1% (v/v) HCl[3,28] or 6% (v/v) $HClO_4$ + 7% (v/v) HCl[41] with 200 μg/ml Ca,[117] 1150 μg/ml Na,[41] or 300 μg/ml K + 2000 μg/ml Sr[3,28] for ionization and interference control, achieving S_r values of 1 and 5% at the 5 and 0.1% concentration levels, respectively.[41] Several workers preferred resolution with HF in polypropylene bottles (120°C) or PTFE autoclaves (150°C) to yield 0.005 to 0.12% (mass/vol) Fe and used H_3BO_3 to complex F prior to analysis.[117,118]

AAS measurements generally used air-C_2H_2, but there was a trend towards N_2O-C_2H_2 in order to prevent interferences from Si and the major matrix elements, Ni, Cr, and Fe. The 279.5 nm line was mainly used but 403.1 nm can be used to avoid dilutions.[41,167]

An AES method for the 0.1 to 1% concentration range in low alloys used 0.5% (mass/vol) Fe in 5% (v/v) HCl, achieving a c_L of 0.02% and a S_r of 0.8% at the 0.22% level using 403.1 nm with N_2O-C_2H_2. Background and overlapping band corrections were required.[12]

AFS used 0.02% (mass/vol) Fe in 0.3% (v/v) HCl + 0.15% (v/v) HNO_3 for 0.1 to 1% in alloys. A S_r value of 2% was achieved at the 0.5% concentration level using 279.8 nm and separated air-C_2H_2.[21]

2. Nonflame

Preliminary GFAAS indicated a c_L of 1 μg/g for alloys.[153]

R. Molybdenum

Molybdenum is residual (< 0.05%) or alloying (0.1 to 10%) in ferrous metals and would be < 10 μg/g for iron ore.

1. Flame

AAS methods for 0.001 to 10% Mo in alloys used 0.1 to 1% (mass/vol) Fe in 2% (v/v) HCl,[110] 10% (v/v) HCl + 5% (v/v) HNO_3,[122] 10% (v/v) $HClO_4$,[3,10,67] 10% (v/v) $HClO_4$ + 10% (v/v) H_2SO_4 + 10% (v/v) H_3PO_4,[10,67] or 10% (v/v) HNO_3 + 3% (v/v) HF + 3% (v/v) HCl,[106] with 1% (mass/vol) NH_4Cl[110] or 3.2 mg/ml Na[122] for interference control in air-C_2H_2, or, alternatively, 1 mg/ml K[106] for ionization control in N_2O-C_2H_2, and achieved a S_r of 0.7% at the 2% concentration level,[110] using 313.3 nm.

For 0.02 to 0.1% Mo, an AES method used solvent extraction from 1.2 *M* H_2SO_4 + 0.25% (mass/vol) α-benzoinoxime and, with an O_2-C_2H_2 total consumption burner, achieved a S_r of 4% with a concentration of 0.05% at 379.8 nm.[95]

S. Nickel

Nickel is a residual (0.01 to 0.3%) or alloy (0.3 to 30%) in ferrous metals, occurring as a minor element (< 0.05%) in iron ore, although some nickel-bearing (< 0.2%) iron ores have been used.

1. Flame

AAS methods for 0.01 to 15% in alloys used 0.1 to 2% (mass/vol) Fe[105,141] in 2% (v/v) HCl,[3,110] 1.5 to 10% (v/v) HCl/0.5% to 10% (v/v) HNO_3,[12,119] 10% (v/v) $HClO_4$,[10] or 0.75% (v/v) H_3PO_4 + 0.75% (v/v) H_2SO_4[92] and achieved S_r values of 0.4 to 0.6% with standard reference samples at the 10% concentration level.

An AAS method for 10 to 5000 μg/g in iron ore used 0.7% (mass/vol) Fe in 10% (v/v) HCl, with 3 mg/ml K which is derived from flux and is not required for interference control.[3]

AAS measurements at 232.0 nm used oxidizing air-C_2H_2, and background measurements were recommended for the lower range.[91] The less sensitive 341.5 and 352.4 nm were used to avoid excessive dilution.[110,167]

An AES method for the 0.01 to 0.2% concentration level in alloys used 0.5% (mass/vol) Fe in 5% (v/v) HCl, achieving a c_L of 0.005 mass% and a S_r of 2% at the 0.05% level using 351.5 nm with N_2O-C_2H_2. Background and overlapping band corrections are required.[12]

An AFS method used 2% (mass/vol) Fe in 30% (v/v) HCl + 15% (v/v) HNO_3 for 10 to 200 μg/g in alloys. For lower ranges, a prior chloroferrate extraction was required, and dilutions were used for higher ranges. A S_r of 2% was achieved at a concentration level of 2300 μg/g, and interferences were not observed at 351.5 nm using Ar-separated air-C_2H_2.[198]

2. Nonflame

Preliminary GFAAS indicated a c_L of 3 μg/g for alloys.[153] For 40 to 400 μg/g in iron ore by GFAAS, Tomlyjanovic and Grobenski[117] used 232.0 nm with a 25-μl aliquot containing 50 μg Fe, 220 μg HCl, 90 μg HNO_3, 1400 μg HF, and 625 μg H_3BO_3, and drying at 100°C (30 sec), ashing at 1200°C (30 sec), and atomizing at 2700°C (15 sec).

T. Niobium

Niobium is used to prevent weld decay (0.02 to 0.1%), to prevent intergranular corrosion in stainless steels (0.1 to 1%), and for permanent magnet alloys (1 to 6%). For iron ore, Nb would be < 10 μg/g.

1. Flame

AAS methods for the 0.05 to 2% concentration range used 2% (mass/vol) Fe in 8% (v/v) HF + 2% (v/v) HCl + 2% (v/v) HNO_3, achieving a c_L of 0.05%.[135] Concentration to 20%[134] or 120%[177] (mass/vol) was achieved by nonresolution of NbC in 8% (v/v) H_2SO_4. Subsequent dissolution to 2% (mass/vol) $(NH_4)_2SO_4$ + 2% (v/v) H_2SO_4[134] or 20% (v/v) HF + 20% (v/v) HNO_3,[177] with 5 mg/ml Al[134] or 7000 μg/ml K[177] for ionization control, and a c_L of 0.01 mass% was found for the concentration range 0.01 to 2%. These methods were inapplicable when all Nb was not present as carbide. AAS measurements at 334.3[134,177] or 405.9 nm[135] used reducing N_2O-C_2H_2.

U. Phosphorus

Phosphorus causes cold-brittleness in steel and is specified to <0.03 or 0.05%; however, alloying amounts (0.15 to 0.4%) harden cast iron and favor thin section castings. Iron ore specifications usually specify P < 0.03 or 0.05%.[18]

1. Flame

The indirect AAS determination of P was achieved (as described in Section IV.c.4) and Mo absorbance was measured at 313.3 nm using N_2O-C_2H_2[160] or air-C_2H_2.[161]

V. Potassium

Potassium is an ultratrace residual in ferrous alloys (0.1 to 50 μg/g) and is < 2000 μg/g in iron ores.

1. Flame

AAS methods for iron ores used 0.03 to 0.3% (mass/vol) Fe in 10% (v/v) $HClO_4$,[3,28,29] 0.5 to 5% (v/v) HCl,[115,166] or 0.75% (v/v) HCl + 0.25% (v/v) HNO_3 + 5% (v/v) HF + 2.5% (mass/vol) H_3BO_3;[117] for the 0.01 to 1.0% concentration range, a S_r of 5% was achieved at the 0.25% level using 766.5 or 769.9 nm and air-C_2H_2. The reviewer suggests that Li or Cs (approximately 1 to 2 mg/ml) would overcome mutual enhancement of alkali metals; La (approximately 1 mg/ml) would be beneficial in certain matrices where significant concentrations of Al(III), SO_4(II), or PO_4(III) are derived from the sample; and insolubles should be recovered and dissolved in a PTFE bomb (150°C)[166] or fused with $Li_2B_4O_7$.

An AES method concentrated to 5% (mass/vol) with a mercury-cathode separation, using HCl media at pH 4 with 100 μg/ml Sr to avoid suppression interferences when determining 1 to 50 μg/g in stainless steel with 766.5 nm and air-C_2H_2.[116]

W. Selenium

Selenium is a residual (< 50 μg/g) or alloy (50 to 3000 μg/g) for improved machinability[204] and for iron ore is < 10 μg/g.

1. Flame

AAS methods for alloys used 1 to 2% (mass/vol) Fe in 10% (v/v) HCl[74] or 1.5% (v/v) H_2SO_4 + 1.5% (v/v) H_3PO_4[204] for the 100 to 3000 μg/g concentration level, achieving a c_L of 30 μg/g at 196.0 nm with air-C_2H_2. Background correction measurements were necessary.[74]

2. Nonflame

An AAS hydride evolution technique for alloys used 20 mg Fe in 17% (v/v) HCl + 0.8% (v/v) HNO_3, with a generation volume of 10 ml and 0.3 g $NaBH_4$ as reductant. A calibration curve is prepared for the sample concentration range 0 to 75 μg/g (c_L = 1 μg/g) (196.0 nm), and a S_r of 3% was achieved for a standard reference sample containing 30 μg/g. The evolved H_2Se was atomized in air-entrained Ar/H_2, and background measurements were not required. The Fe concentration was maintained constant irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and > 0.1% Mo or > 1% Cu interfered.[58]

X. Silicon

Silicon is a deoxidant (0.005 to 0.5%) or alloying element (0.5 to 8%) in ferrous metals, and acid-insoluble Si should be recovered. Iron ore specifications require < 5% Si.[18]

1. Flame

AAS methods for 0.03 to 10% Si in alloys used 0.5 to 1% (mass/vol) Fe in 2% (v/v) H_2SO_4,[126,172] 2% (v/v) H_2SO_4 + 10% (v/v) HCl,[128] 7.5 to 15% (v/v) HCl/2.5 to 5% (v/v) HNO_3,[24,119,172] 10% (v/v) HCl + 10% (v/v) HNO_3 + 10% (v/v) HF,[66] or 10% (v/v) $HClO_4$ + 5% (v/v) HF + 2.5% (m/v) H_3BO_3,[127] with 10 mg/ml Na[66] for ionization control, achieving S_r values of 9 and 2% at the 0.2 and 3% levels, respectively. There was a definite trend from the use of HF to acids of sufficiently weak concentration to avoid hydrolysis of Si, and, in this regard, the existing molecular spectrophotometric methods are being emulated.[205]

AAS methods for iron ore used fusion,[129] autoclave (140 to 150°C),[117,129] or polypropylene bottle (120°C)[118] dissolution to give 0.12 to 1.2% (mass/vol) Fe and used H_3BO_3 to complex F prior to analysis; a S_r of 3% was achieved at the 4% concentration level, and 6 mg/ml Na was used for ionization control.[129]

AAS measurements used 251.6 nm and N_2O-C_2H_2. The general nonuse of ionization control is surprising, and the reviewer suggests that appropriate studies will show the necessity for this, particularly when the Fe concentration is varying.

Y. Silver

Silver is deleterious and causes cracking during rolling of alloys.[206]

1. Flame

An AAS method for alloys used 2% (mass/vol) Fe in 20% (v/v) HCl; for the 5 to 200 µg/g concentration range, a c_L of 1 µg/g was achieved.[206] Solvent extraction of 0.05 to 31 µg/g was achieved from 1-g samples in 1.2 *M* HCl + 0.55 *M* KI media, using 5% (mass/vol) TOPO/MIBK and a c_L of 0.2 µg/g was achieved together with a S_r value of 2% at the 1 µg/g concentration level. Measurements used 328.1 nm and air-C_2H_2.

Z. Sodium

Sodium is an ultratrace residual in alloys (0.1 to 50 µg/g) and is generally < 2000 µg/g in iron ores.

1. Flame

AAS methods for 0.002 to 1% in iron ores used 0.03 to 0.3% (mass/vol) Fe in 10% (v/v) $HClO_4$,[3,28,29] 0.5 to 5% (v/v) HCl,[115,166] or 0.75% (v/v) HCl + 0.25% (v/v) HNO_3 + 5% (v/v) HF + 2.5% (mass/vol) H_3BO_3,[117] and 589.0 or 589.6 nm with air-C_2H_2. The reviewer suggests that Li or Cs (approximately 1 to 2 mg/ml) would overcome mutual enhancement of alkali metals; La (approximately 1 mg/ml) would be beneficial in certain matrices where significant concentrations of Al(III), SO_4(II), or PO_4(III) are derived from the sample; and insoluble residues should be recovered and dissolved in a PTFE bomb (150°C)[166] or fused with $Li_2B_4O_7$.

An AES method concentrated to 5% (mass/vol) with a mercury-cathode separation, using HCl media at pH 4 with 100 µg/ml Sr to avoid suppression interferences when determining 1 to 50 µg/g in stainless steel with 589.0 nm and air-C_2H_2.

AA. Tellurium

Tellurium is a residual (< 50 µg/g) used for improved machinability (100 to 500 µg/g) of alloys and for iron ore (< 10 µg/g).

1. Flame

AAS methods for alloys used 2% (mass/vol) Fe in 10 to 20% (v/v) HCl for the 50 to 1000 µg/g concentration level, achieving a c_L of 30 µg/g at 214.3 nm using air-C_2H_2. Background correction was necessary.[74,207]

2. Nonflame

An AAS hydride evolution technique for alloys used 20 mg Fe in 52% (v/v) HCl + 0.8% (v/v) HNO_3, with a generation volume of 10 ml and 0.3 g $NaBH_4$ as reductant. A calibration curve is prepared for the sample concentration range 0 to 100 µg/g (c_L = 1 µg/g) (214.3 nm), and a S_r of 20% was achieved for a standard reference sample containing 9 µg/g. The evolved H_2Te was atomized in air-entrained Ar/H_2, and background measurements were not required. The Fe concentration was maintained constant irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and > 0.3% Mo or > 0.5% Cu interfered.[58]

BB. Thallium

Thallium is deleterious (1 to 25 μg/g) in alloys used for high-temperature applications.[55]

1. Flame

An AAS method for 0.1 to 25 μg/g in alloys used solvent extraction from 1- to 10-g samples in 2.0 *M* HCl + 0.3 *M* KI with 5% (mass/vol) TOPO/MIBK, achieving a c_L value of 0.1 μg/g when using 276.8 nm and air-C_2H_2.[55]

CC. Tin

Tin is deleterious (1 to 500 μg/g) in alloys causing cracking in welded steel sections[156] and temper brittleness in high alloys.[183]

1. Flame

AAS methods for 50 to 1000 μg/g[3,10] in alloys used 1 to 2% (mass/vol) Fe in 5 to 10% (v/v) HCl[74,208] or 10% (v/v) $HClO_4$,[10] achieving a c_L of 20 μg/g.[74] Background measurements were recommended. AAS pulse nebulization, with 10% (mass/vol) Fe in 35% (v/v) HCl + 15% (v/v) HNO_3, achieved a c_L value of 8 μg/g for the concentration range 10 to 400 μg/g.[53] Solvent extractions achieved c_L values of 0.1[59] or 10 μg/g[183] with 1- to 10-g samples in 1.2 *M* HCl + 0.3 *M* KI using 5% (m/v) TOPO/MIBK[59,60] and 1-g samples of 0.5 *M* HCl + 0.5 *M* KCNS using MIBK.[183] AAS measurements at 224.6 nm used N_2O-C_2H_2; less-used alternative wavelengths were 284.0[3] and 286.3 nm.[53] AFS methods used 1% (mass/vol) Fe in 10% (v/v) HCl for the 10 to 1000 μg/g concentration range to achieve a c_L value of 5 μg/g at 303.4 nm. Si caused enhancement and must be removed during dissolution.[81,101] Argon-separated air-C_2H_2,[81] Ar-O_2-H_2,[81] or air-C_2H_2[101] were used. Air-C_2H_2 was preferred due to the interferences experienced with lower-temperature flames.[101]

2. Nonflame

An AAS hydride evolution technique for alloys used 20 mg Fe in 5% (m/v) tartaric acid + 1.5% (v/v) $HClO_4$ with a generation volume of 15 ml and 0.3 g $NaBH_4$ as reductant. Calibration curves were prepared for the sample concentration ranges 0 to 50 μg/g (c_L = 2 μg/g) (286.3 nm) and 2 to 150 μg/g (235.5 nm); a S_r of 3% was achieved for a standard reference sample containing 400 μg/g. The evolved SnH_4 was atomized in air-entrained Ar-H_2, and background measurements were not required. The Fe concentration was maintained constant, irrespective of alloy composition or the use of smaller aliquots for higher concentrations, and > 2.5% Ni interfered.[58]

DD. Titanium

Titanium is a residual (50 to 1000 μg/g) or alloy (0.02 to 5%) in ferrous metals. Iron ores generally contain 0.01 to 0.2% The acid insoluble residues in alloys and iron ores require dissolution to recover Ti.

1. Flame

AAS methods for alloys used 1% (mass/vol) Fe in 20% (v/v) HCl[3,132] or 10% (v/v) $HClO_4$,[10] with 100 to 500 μg/ml Al for ionization control.[3,132] For the 0.01 to 2% concentration range, a S_r of 3% was achieved. Thomerson and Price[10] claimed that ionization control was not required.

AAS methods for 0.005 to 0.3% in iron ores used 0.12 to 0.6% (mass/vol) Fe in 10% (v/v) HCl[3,28] or 0.75% (v/v) HCl + 0.25% (v/v) HNO_3 + 5% (v/v) HF + 2.5% (mass/vol) H_3BO_3[117] with 2 to 3 mg/ml K for ionization control.

AAS measurements at 364.3 nm used reducing N_2O-C_2H_2.

EE. Tungsten

Tungsten is used for alloying (0.3 to 20%) in ferrous metals.

1. Flame

AAS methods for 0.1 to 20% in alloys used, 0.5 to 1% (mass/vol) Fe, in HCl + HNO_3 + HF,[66,106] + $HClO_4$ + H_2SO_4 + H_3PO_4,[10] or H_2SO_4 + H_3PO_4,[126] with 10 mg/ml Na[66] or 1 mg/ml K[106] for ionization control at 255.1 nm using N_2O-C_2H_2. The Na concentration is unnecessarily high.

FF. Vanadium

Vanadium occurs as a residual (5 to 200 μg/g) or alloy (0.02 to 3%) in ferrous metals. The concentration in iron ore is generally < 0.05%.

1. Flame

AAS methods for 0.005 to 4% in alloys used 0.5 to 1% (mass/vol) Fe in 10% (v/v) $HClO_4$,[10] 10% (v/v) HCl,[3,130] or 10% (v/v) HNO_3 + 3% (v/v) HF + 3% (v/v) HCl[106] with 1 mg/ml K[106] or 100 to 1000 μg/ml Al,[3,130] achieving S_r values of 3 to 4% (0.05 to 2%). Ion exchange onto "Zeo-Karb 225®" from 1 *M* HCl separated V from high-alloy matrices, and elution to 20% (mass/vol) was achieved with 1.8 *M* followed by 4.5 *M* HCl; 3

mg/ml Al was used for ionization control for the concentration ranges 5 to 120 μg/g.[131]

AAS methods for 10 to 5000 μg/g in iron ore used 0.7% (mass/vol) Fe in 10% (v/v) HCl, with 3000 μg/ml K + 500 μg/ml Al for ionization control.[3,28,29]

AAS measurements at 318.4 nm used reducing N_2O-C_2H_2.

An AES method for the 0.01 to 0.3% concentration level in low alloys used 0.5% (mass/vol) Fe in 5% (v/v) HCl, achieving a c_L value of 0.01 mass % and a S_r of 4% at the 0.05% level using 437.9 nm and N_2O/C_2H_2. Background and overlapping band corrections were required.[12]

2. *Nonflame*

Preliminary GFAAS indicated a c_L of 6 μg/g for alloys.[153]

GG. Zinc

Zinc is a residual deleterious element (< 50 μg/g) in alloys. Iron ore specifications limit Zn to <100 μg/g because of refractory damage to iron blast furnaces.[18] Significant concentrations (0.05 to 1%) can occur in pyrites.

1. *Flame*

AAS methods for alloys used 0.2 to 2% (m/v) Fe in 10% (v/v) HCl[74] or 10% (v/v) $HClO_4$.[3] For the 5 to 200 μg/g concentration range, a c_L of 1 μg/g was achieved. Background correction methods were essential.[3,23,74,91]

AAS methods for 0.001 to 1% in iron ore and pyrites used 0.12 to 1.2% (mass/vol) Fe in 10 to 22% (v/v) HCl[3,28,29,124] or 0.75% (v/v) HCl + 0.25% (v/v) HNO_3 + 5% (v/v) HF + 2.5% (m/v) H_3BO_3,[117] with 3 mg/ml Na[124] or K[3] derived from fluxes and not required for ionization control. A S_r of 2% was achieved at the 0.6% concentration level.[124]

AAS measurements at 213.9 nm used air-C_2H_2.

2. *Nonflame*

Preliminary GFAAS indicated a c_L of 0.2 μg/g for alloys.[153]

SYMBOLS AND ABBREVIATIONS

The following symbols and abbreviations have been used.

A	Absorbance
AAS	Atomic absorption spectrometry
AES	Atomic emission spectrometry
AFS	Atomic fluorescence spectrometry
APDC	Ammonium pyrrolidinedithioca bamate
ASTM	American Society for Testing and Materials
c_L	Limit(s) of detection[13]
CVH	Constant voltage heating
EDL	Electrodeless discharge lamp
EDTA	Ethylenedinitrilo tetraacetic acid
GF	Graphite furnace
GFAAS	Graphite furnace atomic absorptio spectrometry
GFAES	Graphite furnace atomic emissio spectrometry
HCL	Hollow cathode lamp
HCl	Hydrochloric acid
ISO	International Organization for Stan ardization
JSA	Japanese Standards Association
MIBK	Methyl isobutyl ketone
OES	Optical emission spectrometry
PTFE	Polytetrafluoroethylene
RF	Radio frequency
s	Standard deviation/s[13]
SAA	Standards Association of Australia
S_r	Relative standard deviation[13]
TCH	Temperature controlled heating
TOPO	Trioctylphosphine oxide
XRFS	X-Ray fluorescence spectrometry

ACKNOWLEDGMENTS

The author thanks The Broken Hill Proprietar Company Limited for providing resources used i the preparation of the review. Appreciation : expressed to various authors who supplied advanc information concerning recent work or approve the use of previously published figures and table: Likewise, the permission of The American Chen ical Society, Elsevier Scientific Publishing Con pany, The Iron & Steel Institute of Japan, Th Chemical Society, Verlag Stahleisen m.b.H Springer-Verlag, Pergamon Press Limited, Intern: tional Scientific Communications Inc., and Societ for Applied Spectroscopy to use copyrighte figures and tables is acknowledged with thanks.

REFERENCES

1. Statistisches Bundesamt, *Met. Bull.* London, 6122, 42 (1976).
2. *World Steel in Figures, 76,* International Iron and Steel Institute, Brussels, 1976.
3. Endo, Y. and Nakahara, Y., *Trans. Iron Steel Inst. Jpn.,* 16, 396 (1976).
4. Ottaway, J. M. and Shaw, F., *Analyst* (London), 100, 438 (1975).
5. Grimm, W., *Spectrochim. Acta Part B,* 23, 443 (1968).
6. Gough, D. S., Hannaford, P., and Walsh, A., *Spectrochim. Acta Part B,* 28, 197 (1973).
7. Gough, D. S., *Anal. Chem.,* 48, 1926 (1976).
8. Hunter, J. K., Ottaway, J. M., and Shaw, F., *Metall. Met. Form.,* 43, 198 (1976).
9. Headridge, J. B. and Smith, D. R., *Talanta,* 19, 833 (1972).
10. Thomerson, D. R. and Price, W. J., *Analyst* (London), 96, 825 (1971).
11. Fernandez, F. J. and Kerber, J. D., *Am. Lab.,* 8, 49 (1976).
12. Fassel, V. A., Slack, R. W., and Kniseley, R. N., *Anal. Chem.,* 43, 186 (1971).
13. IUPAC, *Pure Appl. Chem.,* 45, 99 (1976).
14. Jenkins, R. H. and Jones, C. P., *Proc. Soc. Anal. Chem.,* 9, 266 (1972).
15. Nall, W. R., in *Proc. 29th Chem. Conf.,* British Independent Steel Producers Association, London, 1976, 11.
16. Jones, A. H. and France, W. D., *Anal. Chem.,* 44, 1884 (1972).
17. Frech, W., *Fresenius Z. Anal. Chem.,* 275, 353 (1975).
18. *Iron Ore Manual 1976,* Tex Report Company, Ltd., Tokyo, 1976.
19. Ottaway, J. M., in *Proc. 27th Chem. Conf.,* Corporate Development Laboratory, British Steel Corporation, Sheffield, 1974, 43.
20. Harrison, T. S., *Proc. Anal. Div. Chem. Soc.,* 12, 152 (1975).
21. Japanese Standards Association, JIS G1257, 1975.
22. Rains, T. C. and Menis, O., *Anal. Lett.,* 7, 715 (1974).
23. Kelly, W. R. and Moore, C. B., *Anal. Chem.,* 45, 1274 (1973).
24. Belcher, C. B., in *Flame Emission and Atomic Absorption Spectrometry,* Vol. 3, Dean, J. A. and Rains, T. C., Eds., Marcel Dekker, New York, 1975, 486.
25. ASTM Committee E2 on Emission Spectroscopy, *Methods for Emission Spectrochemical Analysis,* 6th ed., American Society for Testing and Materials, Philadelphia, 1971, E-2 P1, 323.
26. Standards Association of Australia, AS CK18, 1970.
27. ASTM Committee E2 on Emission Spectroscopy, *Methods for Emission Spectrochemical Analysis,* 6th ed., American Society for Testing and Materials, Philadelphia, 1971, E-2 SM2-5, 395.
28. Japanese Standards Association, JIS M8204, 1971.
29. Japanese Standards Association, JIS M8204, 1972.
30. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E350-74, Sections 143–152, 586.
31. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E352-73, Sections 99–108, 638.
32. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E353-73, Sections 127–136, 655.
33. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E351-74, Sections 71–80, 614.
34. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E507–73, 776.
35. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E508–73, 779.
36. Standards Association of Australia, AS K1, Part 25, 1969.
37. Standards Association of Australia, AS 1050, Part 29, 1975.
38. Standards Association of Australia, AS K1, Part 20, 1964.
39. Standards Association of Australia, AS 1673, Part 1, 1974.
40. Standards Association of Australia, AS 1673, Part 2, 1974.
41. Standards Association of Australia, AS 1673, Part 3, 1974.
42. Cobb, W. D., Foster, W. W., and Harrison, T. S., *Analyst* (London), 101, 255 (1976).
43. Ottaway, J. M. and Pradhan, N. K., *Talanta,* 20, 927 (1973).
44. Scholes, P. H., Open Report CDL/CAC/117/73, Corporate Development Laboratory, British Steel Corporation, Sheffield, 1973.
45. Belcher, C. B., *Anal. Chim. Acta,* 62, 87 (1972).
46. Sundberg, L. L., *Anal. Chem.,* 45, 1460 (1973),
47. Ottaway, J. M., *Proc. Anal. Div. Chem. Soc.,* 13, 185 (1976).
48. ISO/DIS 4688, TC102 198E, International Organization for Standardization, Geneva, August 1976.
49. Kerber, J. D., Russo, A. J., Peterson, G. E., and Ediger, R. D., *At. Absorpt. Newsl.,* 12, 106 (1973).

50. Ottaway, J. M. and Shaw, F., Paper A30, in 5th Int. Conf. Atomic Spectroscopy, Melbourne, 1975.
51. Fleming, H. D., *Spectrochim. Acta Part B,* 23, 207 (1967).
52. Taylor, M. L. and Belcher, C. B., *Anal. Chim. Acta,* 45, 219 (1969).
53. Thompson, K. C. and Godden, R. G., *Analyst* (London), 101, 96 (1976).
54. Russell, B. J., Shelton, J. P., and Walsh, A., *Spectrochim. Acta,* 8, 317 (1957).
55. Burke, K. E., *Appl. Spectrosc.,* 28, 234 (1974).
56. Burke, K. E., *Talanta,* 21, 417 (1974).
57. Vassilaros, G. L., *Talanta,* 21, 803 (1974).
58. Fleming, H. D. and Ide, R. G., *Anal. Chim. Acta,* 83, 67 (1976).
59. Burke, K. E., *Analyst* (London), 97, 19 (1972).
60. Thornton, K. and Burke, K. E., *Analyst* (London), 99, 469 (1974).
61. Ashy, M. A., Headridge, J. B., and Sowerbutts, A., *Talanta,* 21, 649 (1974).
62. ASTM Committee E2 on Emission Spectroscopy, *Methods for Emission Spectrochemical Analysis,* 6th ed., American Society for Testing and Materials, Philadelphia, 1971, E415–71, 304.
63. Jacobson, E. F., US NTIS AD Report 731478, Springfield, 1971.
64. Tugane, F., Kamakura, M., and Aoyama, F., *Tetsu To Hagane,* 57, 1192 (1971).
65. Price, W. J., *Met. Mater.,* 8, 485 (1974).
66. Rooney, R. C. and Pratt, C. G., *Analyst* (London), 97, 400 (1972).
67. Thomerson, D. R. and Price, W. J., *Analyst* (London), 96, 321 (1971).
68. Headridge, J. B. and Richardson, J., *Analyst* (London), 95, 930, (1970).
69. Headridge, J. B. and Richardson, J., B.I.S.R.A. Open Report MG/D/421/71, Corporate Laboratories, British Steel Corporation, London, 1971.
70. Special Publ. 260, 1975–1976 ed., National Bureau of Standards, Washington, D.C., 1975.
71. Browner, R. F., *Analyst* (London), 99, 617 (1974).
72. Winefordner, J. D. and Elser, R. C., *Anal. Chem.,* 43, 24A (1971).
73. Fassel, V. A. and Kniseley, R. N., *Anal. Chem.,* 46, 1110A (1974).
74. Barnett, W. B. and Kerber, J. D., *At. Absorpt. Newsl.,* 13, 56 (1974).
75. Willis, J. B., in *Handbook of Spectroscopy,* Robinson, J. W., Ed., CRC Press, Cleveland, 1974, 799.
76. Kahn, H. L., Bancroft, M., and Emmel, R. H., *Res. Dev.,* 27, 30 (1976).
77. Hofton, M. E., Open Report GS/TECH/558/2/76/C, Corporate Development Laboratory, British Steel Corporation, Sheffield, 1976.
78. Thompson, K. C. and Thomerson, D. R., *Analyst* (London), 99, 595 (1974).
79. Barnett, W. B., *At. Absorpt. Newsl.,* 12, 142 (1973).
80. Barnett, W. B., Vollmer, J. W., and De Nuzzo, S. M., *At. Absorpt. Newsl.,* 15, 33 (1976).
81. Ebdon, L., Hubbard, D. P., and Michel, R. G., *Anal. Chim. Acta,* 74, 281 (1975).
82. Barnett, W. B. and McLaughlin, E. A., *Anal. Chim. Acta,* 80, 285 (1975).
83. Nakahara, T., Nishino, H., Munemori, M., and Musha, S., *Bull. Chem. Soc. Jpn.,* 46, 1706 (1973).
84. Winge, R. K., Fassel, V. A., and Kniseley, R. N., *Appl. Spectrosc.,* 25, 636 (1971).
85. Walsh, A., *Appl. Spectrosc.,* 27, 335 (1973).
86. Jones, J. L., Dahlquist, R. L., and Hoyt, R. E., *Appl. Spectrosc.,* 25, 628 (1971).
87. Linde, T. R. and Sitek, G. J., *Mater. Eval.,* 33, 263 (1975).
88. Linde, T. R. and Sitek, G. J., *Iron Steelmaker,* 3, 36 (November 1976).
89. Nall, W. R., *Proc. Soc. Anal. Chem.,* 10, 63 (1973).
90. Snelleman, W., Rains, T. C., Yee, K. W., Cook, H. D., and Menis, O., *Anal. Chem.,* 42, 394 (1970).
91. Endo, Y. and Nakahara, Y., *Tetsu To Hagane,* 59, 800 (1973).
92. Gregorczyk, S., Gralewska, K., and Slabon, J., *Chem. Anal.* (Warsaw), 18, 1065 (1973).
93. Scholes, P. H., *Analyst* (London), 93, 197 (1968).
94. Slavin, W., *Atomic Absorption Spectroscopy,* Interscience, New York, 1968, 37.
95. Goto, H., Kakita, Y., and Namiki, M., *Bunseki Kagaku,* 19, 1467 (1970).
96. Sauer, K. and Nitsche, M., *Arch. Eisenhuettenwes.,* 47, 153 (1976).
97. Sebastiani, E., Ohls, K., and Riemer, G., *Fresenius Z. Anal. Chem.,* 264, 105 (1973).
98. Ambrose, A. D., in Proc. 27th Chem. Conf., Corporate Development Laboratory, British Steel Corporation, Sheffield, 1974, 59.
99. Berndt, H. and Jackwerth, E., *Spectrochim. Acta Part B,* 30, 169 (1975).
100. Manning, D. C., *At. Absorpt. Newsl.,* 14, 99 (1975).
101. Michel, R. G., Ebdon, L., and Hubbard, D. P., *Proc. Soc. Anal. Chem.,* 11, 264 (1974).
102. Rubeska, I., *Anal. Chem.,* 48, 1640 (1976).
103. Fleming, H. D., *Anal. Chim. Acta,* 59, 197 (1972).
104. Cobb, W. D., Foster, W. W., and Harrison, T. S., *Anal. Chim. Acta,* 60, 430 (1972).
105. Condylis, A., *Methodes Phys. Anal.,* 7, 146 (1971).
106. Husler, J. W., *At. Absorpt. Newsl.,* 10, 60 (1971).
107. Lovett, R. J., Welch, D. L., and Parsons, M. L., *Appl. Spectrosc.,* 29, 470 (1975).
108. Marks, J. V., Spellman, R. J., and Wysocki, B., *Anal. Chem.,* 48, 1474 (1976).

09. Yagita, Y., Tanaka, K., Sekiguchi, T., Kanda, M., and Matsumoto, I., *Eisei Kagaku,* 21, 225 (1975).
10. Nall, W. R., Brumhead, D., and Whitham, R., *Analyst* (London), 100, 555 (1975).
11. Epstein, M. S. and Rains, T. C., *Anal. Chem.,* 48, 528 (1976).
12. ISO/DIS TC 102 386E, International Organization for Standardization, Geneva, February 1975.
13. Lucco Borlera, M. and Pradelli, G., *Fonderia Ital.,* 19, 403 (1970).
14. Green, H. C., *Analyst* (London), 100, 640 (1975).
15. Cobb, W. D., Foster, W. W., and Harrison, T. S., *Metallurgia,* 83, 239 (1971).
16. Sobkowska, A. and Basinska, M., *Mikrochim. Acta,* 2, 227 (1975).
17. Tomljanovic, M. and Grobenski, Z., *At. Absorpt. Newsl.,* 14, 52 (1975).
18. Reid, J., Galloway, J. M., MacDonald, J., and Bach, B. B., *Metallurgia,* 81, 243 (1970).
19. Brivot, F., Cohort, I., Legrand, G., Louvrier, J., and Voinovitch, I., *Analusis,* 2, 570 (1973).
20. Endo, Y., Hata, T., and Nakahara, Y., *Tetsu To Hagane,* 55, 216 (1969).
21. Norris, J. D. and West T. S., *Anal. Chim. Acta,* 59, 474 (1972).
22. Wada, K., *Bunseki Kagaku,* 21, 221 (1972).
23. Headridge, J. B. and Sowerbutts, A., *Analyst* (London), 98, 57 (1973).
24. Harrison, T. S., Foster, W. W., and Cobb, W. D., *Metall. Met. Form.,* 40, 393 (1973).
25. Cobb, W. D. and Harrison, T. S., *Analyst* (London), 96, 764 (1971).
26. Jimenez Seco, J. L. and Gomez Coedo, A., *Rev. Metal.* (Madrid), 6, 64 (1970).
27. Nakahara, T., Munemori, M., and Musha, S., *Bull. Univ. Osaka Prefect. Ser. A,* 20, 169 (1971).
28. Thormahlen, D. J. and Frank, E. H., *At. Absorpt. Newsl.,* 10, 63 (1971).
29. Guest, R. J. and Macpherson, D. R., *Anal. Chim. Acta,* 71, 233 (1974).
30. Cobb, W. D. and Harrison, T. S., *Metall. Met. Form.,* 39, 167 (1972).
31. Headridge, J. B. and Sowerbutts, A., *Lab. Pract.,* 23, 99 (1974).
32. Cobb, W. D., Foster, W. W., and Harrison, T. S., *Anal. Chim. Acta,* 78, 293 (1975).
33. Nakahara, T., Munemori, M., and Musha, S., *Bull. Chem. Soc. Jpn.,* 46, 1172 (1973).
34. Martin, M. J., *Analyst* (London), 97, 394 (1972).
35. Thomerson, D. R., *Spectrovision,* 26, 13 (1971).
36. Syty, A., *CRC Crit. Rev. Anal. Chem.,* 4, 155 (1974).
37. Fleming, H. D., private communication, 1976.
38. Goulden, P. D. and Brooksbank, P., *Anal. Chem.,* 46, 1431 (1974).
39. Smith, A. E., *Analyst* (London), 100, 300 (1975).
40. Belcher, R., Bogdanski, S. L., Henden, E., and Townshend, A., *Analyst* (London), 100, 522 (1975).
41. Fernandez, F. J., *At. Absorpt. Newsl.,* 12, 93 (1973).
42. Rains, T. C., private communication, 1977.
43. Maruta, T. and Takeuchi, T., *Anal. Chim. Acta,* 66, 5 (1973).
44. Ottaway, J. M. and Shaw, F., *Analyst* (London), 101, 582 (1976).
45. Ottaway, J. M., *Proc. Anal. Div. Chem. Soc.,* 12, 176 (1975).
46. Fernandez, F. J. and Manning, D. C., *At. Absorpt. Newsl.,* 10, 65 (1971).
47. Lundgren, G., Lundmark, L., and Johansson, G., *Anal. Chem.,* 46, 1028 (1974).
48. Frech, W., *Anal. Chim. Acta,* 77, 43 (1975).
49. Frech, W. and Cedergren, A., *Anal. Chim. Acta,* 82, 83 (1976).
50. Frech, W. and Cedergren, A., *Anal. Chim. Acta,* 82, 93 (1976).
51. Frech, W., *Talanta,* 21, 565 (1974).
52. Adams, M. J. and Kirkbright, G. F., *Can. J. Spectrosc.,* 21, 127 (1976).
53. Shaw, F. and Ottaway, J. M., *Analyst* (London), 100, 217 (1975).
54. Welcher, G. G., Kriege, O. H., and Marks, J. Y., *Anal. Chem.,* 46, 1227 (1974).
55. Yasuda, S. and Kakiyama, H., *Anal. Chim. Acta,* 84, 291 (1976).
56. Ratcliffe, D. B., Byford, C. S., and Osman, P. B., *Anal. Chim. Acta,* 75, 457 (1975).
57. Regan, J. G. T. and Warren, J., *Analyst* (London), 101, 220 (1976).
58. Shaw, F. and Ottaway, J. M., *Analyst* (London), 99, 184 (1974).
59. Kirkbright, G. F. and Johnson, H. N., *Talanta,* 20, 433 (1973).
60. Suzuki, T., Morinaga, H., and Sasaki, A., *Tetsu To Hagane,* 61, 1063 (1975).
61. Baialardo, A. M. and Gomez Coedo, A., *Rev. Metal.* (Madrid), 9, 35 (1973).
62. ISO/R377, 1st ed., International Organization for Standardization, Geneva, 1964.
63. *1975 Annual Book of Standards,* Part 12, American Society for Testing and Materials, Philadelphia, 1975, E59–67, 304.
64. British Standards Institution, BS 1837, 1970.
65. Standards Association of Australia, AS 1213, 1972.
66. ISO TC102 408E, International Organization for Standardization, Geneva, October 1975.
67. Jenkins, R. H. and Jones, C. P., in *3rd Int. Congr. Atomic Absorption Atomic Fluorescence Spectrometry,* Vol. 2, John Wiley & Sons, New York, 1973, 695.
68. Konig, P., Schmitz, K. H., and Thiemann, E., *At. Absorpt. Newsl.,* 9, 103 (1970).
69. Cobb, W. D., Foster, W. W., and Harrison, T. S., *Lab. Pract.,* 24, 143 (1975).

170. Sellers, N. G., *Anal. Chem.*, 44, 410 (1972).
171. Frech, W., Lundgren, G., and Lunner, S. E., *At. Absorpt. Newsl.*, 15, 57 (1976).
172. Hoffert, F., *Cent. Doc. Sider. Circ. Inf. Tech.*, 33, 1147 (1976).
173. Price, W. J. and Roos, J. T. H., *Analyst* (London), 93, 709 (1968).
174. ISO/R439, 2nd ed., International Organization for Standardization, Geneva, 1969.
175. *1975 Annual Book of Standards*, Part 12, American Society for Testing and Materials, Philadelphia, 1975, E50–73, 215.
176. Damiani, M., Tamba, M. G., and Catano, M., *Talanta*, 21, 601 (1974).
177. Schiller, R., *At. Absorpt. Newsl.*, 9, 111 (1970).
178. Belcher, C. B., *Talanta*, 10, 75 (1963).
179. Samsoni, Z., *Banyasz. Kohasz. Lapok Kohasz.*, 109, 68 (1976).
180. Hofton, M. E. and Hubbard, D. P., *Anal. Chim. Acta*, 52, 425 (1970).
181. Matsumoto, I., Takabayashi, T., and Nakamura, I., *Bunseki Kagaku*, 19, 771 (1970).
182. Headridge, J. B. and Smith, D. R., *Lab. Pract.*, 20, 312 (1971).
183. Headridge, J. B. and Sowerbutts, A., *Analyst* (London), 97, 442 (1972).
184. Ichinose, N., *Bunseki Kagaku*, 23, 348 (1974).
185. Kisfaludi, G. and Lenhof, M., *Anal. Chim. Acta*, 54, 83 (1971).
186. Kisfaludi, G. and Lenhof, M., *Anal. Chim. Acta*, 55, 442 (1971).
187. Groupe de Travail Absorption Atomique, *Cent. Doc. Sider. Circ. Inf. Tech.*, 33, 1159 (1976).
188. Luzar, O. and Sliva, V., *Hutn. Listy*, 30, 55 (1975).
189. Atsuya, I. and Sugiura, N., *Bunseki Kagaku*, 23, 1170 (1974).
190. Pederson, B. D. and Taylor, R. W., in *32nd Electric Furnace Conf. Proc.*, Iron and Steel Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1975, 168.
191. Hofton, M. E. and Hubbard, D. P., *Anal. Chim. Acta*, 62, 311 (1972).
192. Wilson, L., *Anal. Chim. Acta*, 35, 123 (1966).
193. Opitz, H., Gappisch, M., Koenig, W., and Pape, R., *Arch. Eisenhuettenwes.*, 33, 841 (1962).
194. Ito, T. and Abeyama, S., *Denki Seiko*, 44, 81 (1973).
195. Timoshenko, N. N., Solomatin, V. T., and Zhukova, M. P., *Zavod. Lab.*, 42, 386 (1976).
196. Barnes, L., *Anal. Chem.*, 38, 1083 (1966).
197. Fogg, A. G., Soleymanloo, S., and Burns, D. T., *Talanta*, 22, 541 (1975).
198. Norris, J. D. and West, T. S., *Anal. Chim. Acta*, 55, 359 (1971).
199. Kinson, K. and Belcher, C. B., *Anal. Chim. Acta*, 31, 180 (1964).
200. Hofton, M. E., Hubbard, D. P., and Vernon, F., *Anal. Chim. Acta*, 55, 367 (1971).
201. Ambrose, A. D., Swingler, D. W., and Clasper, G., *Metall. Met. Form.*, 39, 332 (1972).
202. Matsumura, T., Morooka, R., Kotani, N., and Goto, T., *Tetsu To Hagane*, 59, 1159 (1973).
203. Kurzinski, E. F., *Iron Steel Eng.*, 53, 59 (1976).
204. Peterson, E. A., *At. Absorpt. Newsl.*, 9, 129 (1970).
205. Standards Association of Australia, AS K1, Part 26, 1971.
206. Hofton, M. E., Open Report/GS/TECH/558/1/74C, Corporate Development Laboratory, British Steel Corporation, Sheffield, 1974.
207. Cobb, W. D., Foster, W. W., and Harrison, T. S., *Analyst* (London), 101, 39 (1976).
208. Nakahara, T., Munemori, M., and Musha, S., *Anal. Chim. Acta*, 62, 267 (1972).