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Line Selection and Determination of Trace Amounts of Elements in High-Purity Iron by Inductively Coupled Plasma Atomic Emission Spectrometry

Maria das Graças A. Korn^a; Helena V. Jaeger^a; Adriana C. Ferreira^a; A. C. Spínola Costa^a

^a Instituto de Química, Universidade Federal da Bahia, Salvador, Bahia, Brazil

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**LINE SELECTION AND DETERMINATION OF TRACE
AMOUNTS OF ELEMENTS IN HIGH-PURITY IRON BY
INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION
SPECTROMETRY**

Key words: ICP-AES, Iron, Spectral Interferences

Maria das Graças A. Korn, Helena V. Jaeger, Adriana C. Ferreira and
A. C. Spínola Costa

Instituto de Química, Universidade Federal da Bahia, Campus Universitário de
Ondina, CEP 40170-290, Salvador, Bahia, Brazil

ABSTRACT

The iron matrix effect on the determination of trace amounts of
Zn, Pb, Mn, Cd, Cr, Cu, and Co was studied. An analytical profile of

21 spectral lines of these elements were made, in order to inspect the spectral interference and to study the background in the region of each line using iron solutions of different concentrations. Interference free spectral lines, for some elements, have been recommended to be used for analysis. Recoveries from the iron commercial product spiked with 0.100 μg each of seven analytes are reported. For determination of trace metal a removal of iron by solvent extraction technique prior to the instrumental measurements was required.

INTRODUCTION

Determination of traces of impurities in high purity iron has been demanded in connection with the studies of purification and physical properties of iron [1-4]. The requirements in quality control and analytical specifications of micro-alloyed steels are becoming more and more strict, with the aim of reliably establishing the influence of specific minor elements. Therefore, much effort has been made in developing sensitive and reliable methods which enable trace elemental determination in high purity iron. Several methods have already been described, such as neutron activation analysis [5], atomic

absorption spectrometry [6-9], and atomic emission spectrometry [9-11].

ICP-AES has been widely recognized as a suitable technique for the determination of trace elements, the particular advantages being: the multi-element capability, large dynamic range, and effective background correction. However, several problems have been indicated by researchers (e.g., spectral interferences owing to matrix components, nebulizer blockage owing to the high solids content of solution, or analyte emission enhancement) [12,13]. Severe spectral interferences represent the main limitation of trace analysis by ICP-AES when the analytes must be determined in the presence of high concentrations of elements with a line-rich emission spectra, such as those from uranium, iron, or lanthanide matrices, which must be removed prior to undertaking impurity analyses. The influence of iron rich matrices for the direct determination of trace impurities on the $\mu\text{g/g}$ -levels has been studied in the past few years. Chen and associates [9] measured the detection limits obtained for the determination of trace elements in dissolved iron, and they observed a decrease in the sensitivity and a high spectral background. Ochsenkuhn-Petropulu and Scramel [14] investigated a

preconcentration/separation method for the on-line determination by ICP-AES of gold in iron rich matrices. In that paper an increasing background shift was also observed and high resolution of the used ICP-spectrometer was not enough to overcome this spectral overlapping. In the usual case the impurities must be separated from the Fe matrix before metals determination due to spectral interference, thus various separation methods have been reported. These methods included ion-exchange, co-precipitation, and a variety of solvent extraction techniques [4,11,14-18]. However, references were not found for a systematic study as proposed by this work, where the interference is related to the iron concentration in the sample, and with the selection of spectral lines.

The main goal of the present work was to study spectral interferences caused by the high concentration iron matrix on the determination Zn, Pb, Mn, Cd, Cr, Cu, and Co, which were determined in commercially available iron products.

EXPERIMENTAL

Instrumentation

The instrument used was an Applied Research Laboratory

TABLE 1

Instrumentation and main operating conditions

| | |
|---|-------|
| Frequency/MHz | 27.12 |
| Forward power/kW | 0.65 |
| Reflected frequency/W | < 5 |
| Coolant gas/ L min ⁻¹ | 7.4 |
| Intermediate gas/ L min ⁻¹ | 0.8 |
| Carrier gas/ L min ⁻¹ | 0.8 |
| Observation height/mm above the load coil | 9.0 |

(ARL) Model 3410+ sequential ICP spectrometer (Fisons, Dearborn, MI, USA), with a Czerny-Turner type monochromator. The system used a computer controlled stepping motor to position the diffraction grating relative to a Minitorch. For the nebulization a concentric pneumatic nebulizer (Meinhard type) was employed, with a sample flow rate of 2.3 mL min⁻¹ (Gilson Miniplus 2 peristaltic pump). The resolution of the spectrometer was 0.011 nm, as given by the manufacturer (holographic grating, 2400 grooves/mm). The main operating conditions are given in Table 1.

Reagents

Stock solutions were prepared by dissolution of pure metals or reagent grade chemicals in diluted acid and deionized water.

Reference solutions were prepared by appropriate dilutions of the stock solutions in deionized water and were stored in polyethylene bottles.

Iron pure 99.8% (IPT 73, Brazil) was used to prepare stock iron solutions. HCl was of analytical grade reagent.

Sample preparation

Iron solution (A): Dissolve 5.00 g of Iron Reduced GR-ART 3819 (Merck) in 20 mL of concentrated hydrochloric acid, with heating, and then slowly add 5 mL of concentrated nitric acid, dilute to volume with water in a 100 mL standard flask.

Iron solution (B): Dilute the Titrisol Iron Standard solution (Merck) to volume with water in a 100 mL standard flask.

General procedure

As a first step, wavelength profiles are acquired for the synthetic aqueous solutions containing the analytes with and without $5.000 \mu\text{g mL}^{-1}$ of iron and one each for the blank. For a selected spectral line, four scans were recorded and reproduced in the same figure. The same procedure was used for all the lines.

In a second step, to confirm the influence of the iron on the metal determinations, increasing amounts of iron were added and the analytical signals were measured for some important wavelengths. Detection limits for the elements in acid medium and in the iron matrix were calculated for the best emission lines.

In a third step, the simultaneous analysis of some metals were made without separation of the matrix and with iron extraction before the metals determination in ICP-AES. For determination of elements, with separation, removal of the iron matrix by solvent extraction of its chlorocomplex with MIBK is a suitable way.

Portions of iron solution were shaken with a 0.5 mL solution of the metals ($5\mu\text{g mL}^{-1}$), 20 mL of 7 M hydrochloric acid, and 20 mL of methyl isobutyl ketone in a separatory funnel for 1 min. The organic phase was discarded and the aqueous phase was diluted to 25 mL for the metal determinations.

RESULTS AND DISCUSSION

Investigation of spectral lines

Several examples have been published [19, 20] which illustrate the problems encountered with the prediction of spectral interferences

TABLE 2

Spectral lines of the elements selected for spectral scans

| ELEMENT | SPECTRAL LINE | | |
|---------|-----------------|---------|----------|
| | (nm) | | |
| Zn | 213.856 | 206.191 | 334.499 |
| Pb | 220.353 | 216.999 | 283.306 |
| Mn | 257.610 | 259.373 | 293.306* |
| Cd | 214.438 | 228.808 | 226.505 |
| Cr | 205.552 | 267.716 | 283.562 |
| Co | 238.892 | 228.616 | 237.862 |
| Cu | 324.754* | 224.700 | 327.396 |

*Fe interference free spectral line

The most sensitive lines are printed in bold [21, 22]

as a result of incompleteness of the available wavelength tables. Consequently, when a new matrix is investigated, it is absolutely necessary to carry out wavelength scans in the vicinity of the analysis lines to check the presence or absence of interfering lines. Using the data of Winge et al [21, 22] we have selected the three most sensitive lines for each element and emission spectra were recorded for solutions of iron and for solutions spiked with the metal of interest. For comparison, standard solutions containing only the metal were also investigated. Table 2 shows the 21 lines selected for spectral scans.

Some of the prominent analyte lines studied are free from Fe spectral interferences (Table 2). These wavelengths can be used for

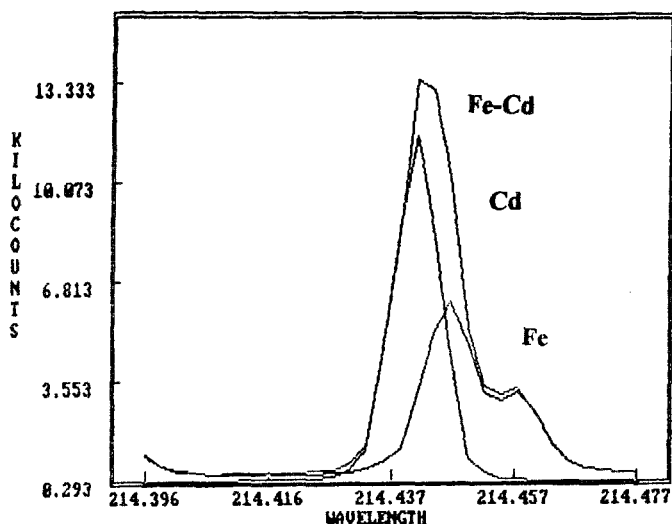


FIG. 1 Typical scans. spectral interference due enhancement of background level Cd 214.438nm.

the determination of small amounts of these elements in iron-rich material.

Three types of spectral interferences have been observed: (a) enhancement of background level due to the matrix; (b) partial overlap by the wing of another line, and (c) direct spectral overlap. Typical scans are presented in Figures 1, 2 and 3.

(a) Enhancement of background level due to the matrix

Table 3 lists the analytical emission lines that presented pronounced background enhancement. This behavior can be attributed to neighbor lines of Fe.

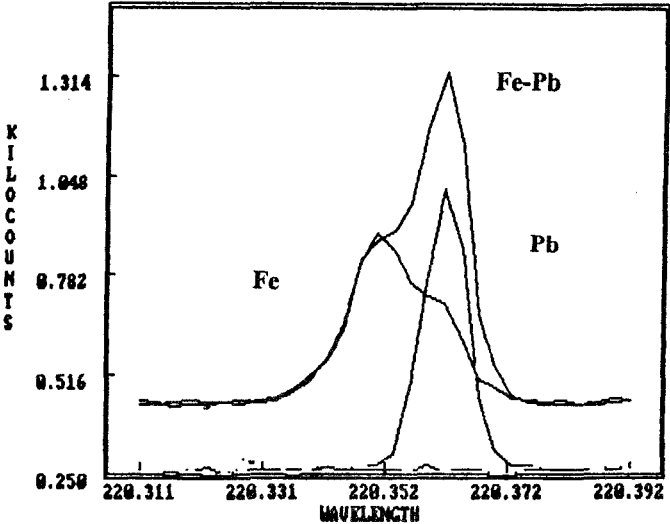


FIG. 2 Typical scans. spectral interference due partial overlap by the wing of another line Pb 220.350

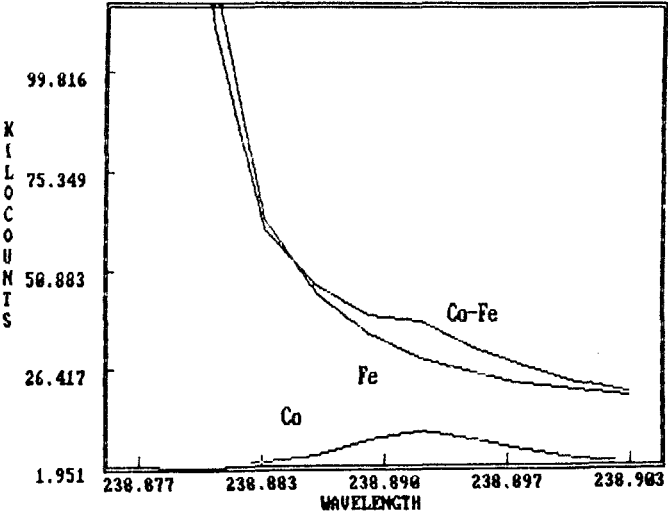


FIG. 3 Typical scans. spectral interference due direct spectral overlap Co 238.892.

Table 3

Lines with background enhancement interference and spectral overlap due to Fe matrix

| Elements | Background Enhancement | Spectral Overlap |
|----------|---------------------------|---------------------------|
| | <i>Spectral Line (nm)</i> | <i>Spectral Line (nm)</i> |
| Cd | 228.808 | 226.502 214.438 |
| Co | 228.616 | 238.892 237.862 |
| Cr | 205.552 267.716 | 283.562 |
| Cu | 327.396 | 224.700 |
| Mn | ----- | 257.610 259.973 |
| Pb | 220.350 | 216.999 283.862 |
| Zn | ----- | 213.856 334.502 |

(b) Partial overlap by the wing of another line

When inter-element interference is due to partial spectral line overlap - as for Zn II 206.191 nm and Cd II 214.438 nm by a nearby Fe line - then the problems of making inter-element corrections are more difficult. The reason for this is that small changes in the profile setting of the spectrometer (position of the spectrometer entrance slit) can severely alter the degree of interference on the analyte line.

(c) Direct spectral overlap

Direct spectral overlap interferences, exemplified by the

interference of iron upon Co II 238.892 nm, Zn I 213.856 nm, and Pb I 283.306 line, have been a continuing problem in emission spectroscopy. Other analytical emission lines that presented direct spectral overlap are listed in Table 3.

Effect of iron concentration

In order to establish the magnitude of spectral interference, the gross peak intensities of the prepared iron solutions (50, 100, 300, 500 and 1000 $\mu\text{g mL}^{-1}$) and the intensities due to blank solution 1% (v/v) HCl in deionized water were measured at prominent lines. Since there was a large variation in the magnitude of interferences for different elements, the higher relative emission intensity was taken as 100 and it was possible to show the interferences for the analyte elements simultaneously. Figure 4 shows a typical graphical representation of the magnitude of spectral interferences at different iron concentration levels for, Zn I 213.856, Pb I 220.353 nm, Mn II 257.610, Cd II 214.438 nm, Cr II 205.552, Cu I 324.754, and Co II 238.892 nm. It can clearly be seen that the spectral background was found to increase with the iron concentration except for Cu, as it was expected. The matrix has a significant effect on the intensity and

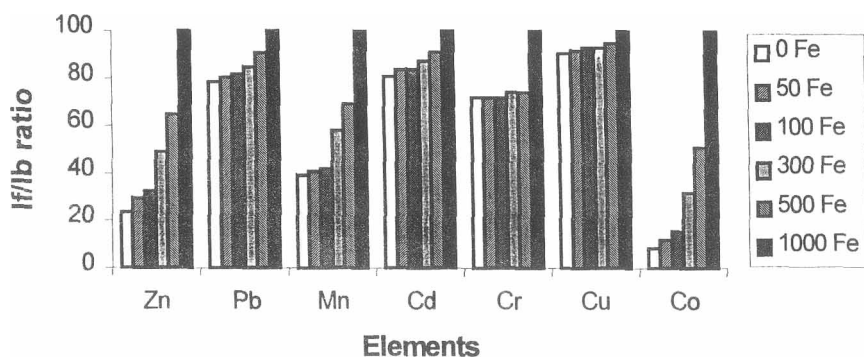


FIG. 4 Effect of different iron concentration levels on the emission intensities of various analytical lines.

nature of the background when the sample was introduced into the plasma. It has modified the aerosol generation processes and the excitation mechanisms in the plasma through inter-element effects.

Limits of Detection

Optimum line selection for trace analysis implies that the prominent lines are selected representing the minimum value of the true limit of detection (LOD), i.e. those lines with the fewest overlapped neighboring lines, and background interference signals, in the presence of the matrix. For a line-rich spectrum, the dependence of the background intensity on wavelength differs drastically from that of the pure solvent. The largest enhancements being found in regions

with intense lines. Consequently, the limits of detection of the prominent analyte lines located in those regions will be substantially different from those found in the pure solvent, where no direct line overlap occurs with the lines of the matrix [10,11].

It is difficult in some cases to measure the limits of detection directly because the so-called pure iron contains traces of other elements such as: Ni, Mn, Pb, Co, and Cr. Accordingly, selected elements were measured directly in the presence of a matrix and those values were compared with aqueous limits of detection. The limits of detection were defined as the concentration of analyte which produces a signal equivalent to a 95% confidence limit of the background variation as determined on a set of 30 measurement [7].

Limits of detection were determined for the best emission lines in acid medium, with and without the iron matrix. The mean values calculated for LOD are summarized in Table 4. The iron matrix raises the real LOD in comparison with the aqueous solution. High concentrations of iron decreased the sensitivity due to the uncompleted evaporation of particles of high salt content, and due to the ineffective nebulization. Thus, in addition to the above-mentioned spectral interferences, other possible sources of interference included

TABLE 4

Limits of detection (LOD) for aqueous solution and Fe solution concentrations of 5 mg mL^{-1} for the best lines Zn, Pb, Mn, Cd, Cr, Cu, and Co

| ELEMENT | SPECTRAL LINE (nm) | LOD Aqueous solution ($\mu\text{g L}^{-1}$) | LOD Fe solution ($\mu\text{g L}^{-1}$) |
|---------|--------------------|---|--|
| Zn | 213.856 | 6 | 25 |
| Pb | 220.353 | 37 | 59 |
| Mn | 257.610 | 5 | 5 |
| Cd | 214.438 | 10 | 26 |
| Cr | 205.552 | 6 | 6 |
| Cu | 324.754 | 37 | 39 |
| Co | 238.892 | 8 | 132 |

the matrix effects: nebulization interferences, transfer and desolvation interferences, and atomization and volatilization interferences [13].

Trace analysis of commercial high-purity iron

Precision and accuracy of the method have been investigated by performing the analysis of two commercially available samples of high-purity iron. In order to confirm the presence of interference from the matrix by quantitative analysis; Zn, Pb, Mn, Cd, Cr, Cu, and Co were determined. The ICP-AES direct measurements and measurements after extraction were performed.

TABLE 5

Determination of elements ($\mu\text{g mL}^{-1}$) in commercial high-purity iron.

| Elements | Direct determination | | After separating matrix | | | |
|----------|----------------------|-------------------|-------------------------|----------|-------------------|----------|
| | Iron Solution | Iron Solution | Iron Solution | Recovery | Iron Solution | Recovery |
| | A | B | A | % | B | % |
| Pb | 0.654 \pm 0.001 | - | 0.107 \pm 0.007 | 107 | - | - |
| Cd | 0.160 \pm 0.002 | 0.110 \pm 0.001 | 0.099 \pm 0.003 | 99 | 0.088 \pm 0.003 | 88 |
| Co | 5.655 \pm 0.018 | 1.749 \pm 0.004 | 0.105 \pm 0.008 | 105 | 0.103 \pm 0.004 | 103 |
| Cu | 0.112 \pm 0.001 | 0.134 \pm 0.002 | 0.092 \pm 0.006 | 92 | 0.108 \pm 0.003 | 108 |
| Mn | 0.165 \pm 0.001 | 0.153 \pm 0.005 | 0.103 \pm 0.007 | 103 | 0.098 \pm 0.005 | 98 |
| Cr | 0.135 \pm 0.004 | - | 0.107 \pm 0.002 | 107 | - | - |
| Zn | - | 0.242 \pm 0.008 | - | - | 0.103 \pm 0.008 | 103 |

The results reported in Table 5, confirm the presence of an interference effect, as the concentration of metals in the spiked samples are different with and without extraction. Therefore, the direct determination of Zn, Pb, Mn, Cd, Cr, Cu, and Co in iron matrix is not possible. Tests showed suitable recoveries for the elements from the Titrisol Iron Standard solution (Merck), and the Iron Reduced GR –ART 3819 (Merck) pure iron samples after matrix separation.

CONCLUSIONS

Iron is known to have line-rich emission spectra. As a result,

serious spectral interferences must be expected. An interference study was carried out for the determination of minor and trace concentrations of metals in high-purity iron and iron base alloys by ICP-AES. Spectral interferences were investigated through spectral scans in the vicinity of the analyte channel. Significant spectral interferences, due to enhancement of background or direct overlap, were found for Zn, Co, Pb, and Cd at all the lines selected. The determination has been carried out using a separation method. The method proposed is suitable for the determination of Zn, Pb, Mn, Cd, Cr, Cu, and Co in iron samples.

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