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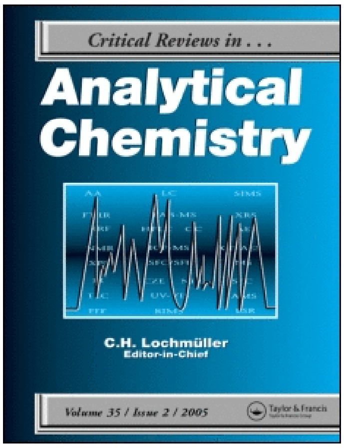

Critical Reviews in Analytical Chemistry

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

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To cite this Article Kiesl, Wolfgang and Grass, Friedrich(1984) 'Analysis of Terrestrial and Extraterrestrial Materials', Critical Reviews in Analytical Chemistry, 15: 2, 119 — 161
To link to this Article: DOI: 10.1080/10408348408542777
URL: http://dx.doi.org/10.1080/10408348408542777

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ANALYSIS OF TERRESTRIAL AND EXTRATERRESTRIAL MATERIALS

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I. INTRODUCTION

The purpose of analytical chemistry, which deals in fact with the analysis of terrestrial and extraterrestrial materials, is to gain information about the qualitative and quantitative composition of substances, that is, to find out what a substance is composed of and exactly how much.

According to the title of this contribution, analytical chemistry has to be considered as a neighboring branch of geochemistry, and we summarize the tasks of the latter as follows. "Geochemistry studies the distribution laws of the chemical elements and isotopes of the earth, in the past and at present." Cosmochemistry deals, according to the geological object of investigation, with the chemistry of the extraterrestrial matter. But geochemistry may also be considered a branch of cosmochemistry.

Since we are presenting the contribution of analytical chemistry to geochemistry, we have to focus on the studies of the quantitative distribution of the chemical elements and isotopes in the individual terrestrial and extraterrestrial materials. Therefore, the main requirements of the analytical data obtained must be accuracy and significance. It should be noted here that accuracy of results does not mean the overall accuracy of a certain method, but the accuracy of individual measurements expressed, e.g., as the double standard deviation of these single values from the true value. To carry out a correct and reliable analysis may be a very difficult and time-consuming operation and is not as easy as sometimes supposed, even in the case of a well equipped laboratory. The main problems arise from the fact that analytical work is possibly done on samples which may not be completely representative, cannot be related to anything significant, or have been contaminated in collection or preparation.

Some decades ago it was proposed that, ideally, the geochemist should be trained in geology and analytical chemistry. This in practice was not always possible and is wishful thinking at present, since an analytical chemist may be involved in electronics, interpreting spectra and other instrumental data, developing and evaluating new procedures or modifying old ones, separating simple and complex mixtures, and writing computer programs. It is not likely that any one analytical chemist will be an expert in all of these areas.

This review therefore will deal with those steps of analytical chemistry required to reach satisfactory results, such as sampling, preparating of sample, and analytical procedures as well. Consequently it is the main goal of this contribution not to describe principles of the physical methods listed but to discuss today's best approximations to a solution of a geochemical and cosmochemical problem under the heading of the particular physical method. It should be noted again that this review deals with the most frequently applied methods of geochemistry and cosmochemistry. There are other techniques which are sporadically used but nevertheless are of considerable value, such as ion selective electrode techniques, polarography, fluorimetry, etc.

It stands to reason that analytical separation techniques discussed in the text are selected from innumerable ones on the basis of frequency used in analytical chemistry of extraterrestrial and terrestrial materials, general applicability, time consumption, etc. and therefore are far from being complete. Usually, detailed procedures are described in periodicals such as the *Journal of Radioanalytical Chemistry, Analytical Chemistry, Chemical Geology, Geochimica et Cosmochimica Acta, Earth and Planetary Science Letters, Fresenius Zeitschrift für Analytische Chemie, Microchemica Acta, Monatshefte für Chemie,* etc.

II. GENERAL REMARKS

A. Sampling

Sampling is one of the basic operations common to all analytical procedures. It could be defined as the operation of removing a part, convenient in size for testing, from a whole which is of much greater bulk, in such a way that the proportion and distribution of the qualities to be tested are the same in both the whole and the part removed, the latter being called the sample.

Of course the sample should be a complete representative of the whole and this is practically never fulfilled when heterogeneous mixtures are sampled. And in fact, apart from few exceptions, we deal with more or less complex materials when considering terrestrial and extraterrestrial materials. Elements of sampling are:

1. Precise definition of the qualities to be tested
2. Character of the quality under test

3. Character of the material to be sampled
4. Relation of the quality to be tested to the material to be sampled
5. Character of the sample necessary to supply the information as to the quality about which information is desired
6. Degree of accuracy necessary
7. Way in which the parent lot occurs
8. Sample size required for testing and to satisfy the standard of accuracy and the degree of assurance
9. Method of taking the sample, and consequently mechanism for taking the sample

Most of these factors are discussed in detail in an outstanding article by Behre,[1] in which broad scope is given to the sampling theory. A theoretical and practical survey on sampling has been given recently by the GDMB.[2] The publication deals predominantly with sampling of ores, metals, liquids, and gases.

In practice, the collection of a representative sample usually depends upon the geologist's intimate knowledge of the rocks and their relationships, focusing for the moment on terrestrial materials. Referring to this, the analyst, or especially the geochemist, should accompany the field man, as routine field work and specimen collection may omit precautions desirable in detailed collecting for geochemical study. Valuable instructions are to be found in articles by Wagner and Brown[3] as well as Pietrzyk and Frank.[4] The desirable amount for collecting rocks, veinstones, and minerals is in any case much larger than the geological hand specimen. An indication of the ideal amounts required, assuming the rock body to be homogeneous and the rock grains equidimensional, is approximately 5000 g for pegmatitic rocks (grain size ~ 3 cm), 2000 g for coarse-grained rocks (grain size 1 to 3 cm), 1000 g for medium-grained rocks (1 to 10 mm), and 500 g for fine-grained rocks (0 to 1 mm).

Special sampling methods are necessary for composite samples made up of many specimens of about equal size. In that case, Shaw and Bankier[5] recommend separation of the constituents and averaging the results, because total analysis has little merit for scientific investigation. Unconsolidated sediments can be collected more easily than the solid rocks. Plastic rocks such as clays have to be cut out simply with a knife, as described by Milner.[6] However, the collection of sediments from the sea floor requires special devices.

Different techniques are employed for sampling liquids and gases. Heterogeneous mixtures such as emulsions, suspensions, or aerosols require statistical handling. Additional complications arise if the liquid mixture contains volatile components or dissolved gases, as for example when dealing with hydrothermal processes.

Atmospheric sampling is much more difficult. Factors such as wind, pollution, or rain are variables which are not easy to overcome or control. Again the type of sampling method that is selected depends on the chemical and physical properties of the substances in the atmosphere that are being determined. Most meaningful from the viewpoint of geochemistry, but at the same time most difficult to collect, are gases taken directly from volcanic vents at high temperatures. Naughton et al.[7] have improved a method developed by Jaggar, Day, and Shepherd between 1912 and 1924. It should be mentioned that the Halemaumau (Hawaii) samples analyzed by Shepherd[8] and Jaggar[9] are still among the best representatives we have of the composition of uncontaminated magmatic gases as shown by Williams and McBirney.[10]

Sampling of extraterrestrial materials is a crucial problem, nearly ignored by scientists working on meteorite samples, and absolutely neglected during investigations on moon samples. It is a remarkable fact that no single contribution during the 12-year publication period of the Proceedings of the Lunar Science Conferences deals with the influence on the reliability of analytical data due to sampling of moon material. It should be noted here that sampling on the moon has been done quite correctly in many cases, but final distribution of material for analytic purposes suffered with respect to representative samples. Instructive articles on sampling techniques on the moon are given by Mühlberger et al.,[11] Vinogradov,[12] and Heiken et al.[13]

Of course it is not convenient to apply, in full, elements of sampling as described for terrestrial material, to extraterrestrial matter because, in addition, two main factors have to be taken into consideration: that is, restricted material-amounts available and/or material tends to be extremely valuable or even expensive.

However, meteorites have been divided into stony meteorites, stony-iron meteorites, and iron meteorites. In general, heterogeneity increases in this direction although we have to consider marked differences with respect to terrestrial rocky matter. Most of the stony meteorites contain minerals of different specific weight such as silicates, troilite (FeS), and metallic grains (Ni-Fe). Troilite and Ni-Fe are occasionally heterogeneously distributed throughout the silicate matrix. In addition, certain iron meteorites are comparable to terrestrial composite samples in containing sulfide nodules with irregular distribution throughout the metal phase.

Fortunately, lunar samples are comparatively simple. Roughly, lunar material can be divided into crystalline igneous rocks, which range from very fine-grained to medium-grained (in rare cases containing crystals more than 1 cm in diameter); into breccias, ranging from fine-grained microbreccias to clasts containing large fragments of igneous rocks; and soils, which are loose mixtures of crystalline grains with larger aggregates, glassy fragments, and trace amounts of metallic iron particles, obviously of meteoritic origin.

In any case, sampling will depend mainly upon the analytical problem, although it should be mentioned that due to the outstanding character of some materials, the analyst should be prepared to gain maximum information on minimal sample quantities.

B. Preparation of Sample

Apart from gaseous or liquid materials, solid samples are usually prepared for analysis as fine powders. Several operations are necessary including crushing, sieving, sample-splitting, phase or mineral separations until the materials are ready for weighing, and final analytical processing. No matter how many of these steps definitively are applied, each one may give rise to contamination. When dealing with these aspects we restrict discussions to physical operations as well as to small-scale methods used in the laboratory; disregarding for the moment chemical phase- or mineral-separations.

Crushing of the solid sample is necessary to reduce size to the desired grain size. As shown by Wagner and Brown,[3] very different methods are in general use, as, e.g., geological hammers, steel jaws in a rock-splitting machine, hand percussion mortars, hydraulic rock-crushers, mechanically driven roller-crusher, etc.

It should be noted that any grinding action is more liable to produce contamination than straight crushing. Moreover, powder loss must be kept to a minimum, for softer minerals form finer powder more rapidly and loss of this will change the overall composition. In general, the analyst should use the coarsest material he can suitably decompose by chemical methods, because crushing to very fine grain sizes also may result in the introduction of errors due to oxidation of ferrous iron and increase of hygroscopic water or expulsion of water from hydrous minerals, although these effects may be reduced by grinding in a nonoxidizing medium, such as absolute alcohol, acetone, or ether.

Information on the effects of contamination using different materials is given in Koch and Koch-Dedic.[14] Using steel mortars, serious effects are due to contamination with Fe, Mn, Cr, V, Ni, Cu, and Mo. If ceramic mortars are applied, contamination with Mg and Ti could occur. Contamination is nearly negligible when using mortars of agate.

Although certain special techniques are recommended for preparation of powders such as drilling with tungsten-carbide drills, it should be mentioned that this may lead to considerable complications, especially during instrumental neutron activation analysis, because W produces W-187 during neutron irradiation. This 24-hr half-life isotope hinders or even prevents the evaluation of short-lived isotopes in the low energy γ-range. That means, although the fact of contamination is recognized and possibly of no relevance to the literal geochemical problem, one observes a significant and undesirable influence during estimation of constituents. Therefore, composition of all materials used during preparation of samples should be known, a condition not always easy to meet.

After or during crushing, materials are normally sieved, not only to ensure specified grain sizes, but also to speed up the crushing process as well as to minimize errors attendant upon excessive pulverization. Most widely used materials for sieving devices are silk or synthetic products, being free from undesirable contaminating effects.

Sieving of extraterrestrial material on the other hand can be much more complicated because even minimal loss of substance has to be avoided. Thus sieves are usually coated to prevent electrostatic effects. If the coating material is, for example, gold, noble metal contents are highly suspect if concentration ranges expected are <1 ppm.

Sample splitting using sample-splitters are applied mainly during investigations of terrestrial material, where large amounts of powdered material has to be reduced in weight for analytical purposes. Whatever method is used today it is believed this preparation method is less responsible for contamination effects. More detailed information on these important subjects is given by Schroll.[15]

It is frequently required that some of the constituents for individual analysis be separated. This can be done mechanically using a drill or mounted needle or by simple hand picking. The ease with which separation can be carried out depends upon the frequency of the phase of interest in the sample, its grain size, and the difference between certain of its physical properties and those of the other constituents. In general, it is the purpose of a mineral or phase separation to study the distribution of elements among the separated constituents, so contamination effects already described are less important. Special care should be directed to impurities of the minerals or phases separated, as for example on inclusions of other minerals or mineral intergrowths; thus, in any case, microscopic inspection should be used. The intergrowths, however, may be due to the subsolidus unmixing of originally homogeneous phases and further correction of the analytical results is not necessary.

If none of the techniques described is applicable, magnetic separation or separation by dense liquids is recommended. Whereas certain technical problems have to be considered in the application of a magnetic separation, contamination effects are common when using dense liquids for mineral separation. When using bromoform, tetrabromoethane, or methylene iodide, remarkable interferences are observed if instrumental neutron activation analysis subsequently is applied, due to the formation of Br-82 (Half-life 35.87 hr), Br-80 (17.6 min), Br-80m (4.38 hr) as well as I-128 (25.4 min). To avoid these interferences it is necessary to use processed and freshly distilled solvents. Finally, the separated minerals should be washed by large quantities of acetone. If, however, activation analysis is the method of choice for investigation after dense liquid separation, it is best to use Clerici-solution, because Tl will not give rise to radioactive nuclides interfering with the evaluation of γ-spectra.

III. ANALYTICAL PROCEDURES

A. Activation Analysis

This method involves the formation of an artificial radionuclide from a stable nuclide by bombardment with thermal neutrons or high-energy particles such as neutrons;

Table 1
NAA SENSITIVITY LIMITS[a]

Element	Isotope ($T_{1/2}$)	A (10^{-9} g)	B (10^{-9} g)
Na	Na-24; 14.97 hr	0.080	1.7
Sc	Sc-46; 83.9 d	0.067	9.7
Mn	Mn-56; 2.57 hr	0.0069	0.029
Co	Co-60m; 10.47 min	0.0061	0.0062
	Co-60; 5.24 y	1.2	180.0
Rh	Rh-104; 44 sec	0.0012	0.0012
	Rh-104m; 4.4 min	0.014	0.014
Ag	Ag-108; 2.3 min	0.0078	0.0078
	Ag-110m; 253 d	3.8	550.0
In	In-116m; 53.99 min	0.0013	0.0024
La	La-140; 40.22 hr	0.031	1.6
Ce	*Ce-141; 32.51 d	3.8	530.0
	*Ce-143; 33 hr	2.3	108.0
Pr	Pr-142; 19.2 hr	0.022	0.60
Nd	Nd-147 ;11.06 d	2.4	300.0
Sm	Sm-153; 47.1 hr	0.0075	0.58
Eu	Eu-152m; 9.2 hr	0.00038	0.0052
	*Eu-152; 12.5 y	0.06	9.0
Gd	Gd-159; 18.0 hr	0.27	7.0
Tb	Tb-160; 72.3 d	0.099	14.0
Dy	Dy-165; 139.2 min	0.00046	0.0018
Ho	Ho-166; 27.3 hr	0.0047	0.18
Er	Er-171; 7.8 hr	0.21	2.4
Tm	Tm-170; 129 d	0.065	9.6,
Yb	Yb-175; 101 hr	0.024	2.2
	*Yb-169; 30.7 d	0.45	63.0
Lu	Lu-177; 6.75 d	0.0059	0.65
Re	Re-188; 16.7 hr	0.0073	0.18
	Re-186; 88.9 hr	0.0095	0.84
Ir	Ir-192; 74 d	0.016	2.4
	Ir-194; 19.0 hr	0.0040	0.11
Au	Au-198; 2.697 d	0.0043	0.32

Note: *—completed by the author for commonly used isotopes.

[a] Flux 10^{13} n/cm^2 · sec, 10 dps, irradiation time A = 150 hr; B = 1 hr.

protons, or α-particles. Activation analysis using electron and photon irradiations is also carried out, although neutron activation with thermal neutrons is predominantly performed concerning nuclear analytical techniques applied on terrestrial and extraterrestrial materials.

The so called neutron-capture gamma-ray analysis is still the best technique for determining exotic elements in the minor and trace element range. There are few methods that compete in sensitivity and accuracy with NAA, viz. mass spectrometric isotope dilution and inductive coupled plasma spectrometry. The main advantage of the nuclear technique is the fact that sensitivity limits can be fixed by the chemist via neutron flux and irradiation time during activation in a nuclear reactor. For gamma-ray measurements, a high resolution detector in connection with a multi-channel system is needed. Table 1 contains sensitivity limits in units of 10^{-9} g of some elements with low detection limits, which will give rise to ten counts per second when irradiated in a thermal neutron flux of 10^{13}n/cm ^{2}/sec for two irradiation times, mostly applied in the analysis of geologic material as calculated by Winchester.[16]

These data are subject to change since the cross section and the neutron flux are both functions of neutron energy, and the activity measurements require knowledge of the efficiency of the detector. In addition, it should be mentioned that sensitivity limits usually calculated this way are not strictly correct, because gamma decay abundances have not been taken into consideration. This means, e.g., in the case of Pr (gamma decay abundance ~ 3.7%), sensitivity limit should be raised by a factor of 27.

It is seen that, among others, the Rare Earth Elements (REE) are included in the table, a group of elements of considerable interest of geochemical and cosmochemical studies. Due to the outstanding significance of these elements, the author will draw special attention to analytical techniques applied for REE.

As will be shown later, sensitivity limits should be considered with care. These can be achieved only by selective separation steps of the element under consideration from the matrix elements. A more or less pronounced interference from matrix elements is avoided by the development of radiochemical group separations, where the desired elements or elemental groups are removed from the matrix. These elements or groups can be separated after or before irradiation. In the latter case, special attention has to be directed to contamination effects: A loss in sensitivity, however, in the order of one or more decimals, has to be considered when an instrumental technique is applied and matrix effects can not be avoided. Finally, in special cases of rare and valuable materials, combined analytical nuclear techniques are generally applied. Examples will be given below.

It is worth mentioning that the most sophisticated separation steps have been developed in the late 1960s for the determination of a wide spectrum of elements in lunar samples, but these techniques rarely have been applied to terrestrial samples and geochemical problems if we neglect applications to geological standard rocks frequently used as secondary standards.

Beyond the advantages of activation analysis, a remarkable effect is often disregarded by many investigations. Since sample weight for activation analysis is very rarely more than 1 g, minute grains of less frequently distributed minerals or phases will lead to nonrepresentative results. The smaller the sample weight (analysis of moon samples is usually done on milligram quantities) the more important is the effect if a minor or trace element is a major constituent of a minor phase (Zr in rare grains of zircon), or is a minor constituent of a minor phase (Cl in rare grains of chlorapatite), or is a constituent of an intergranular film (water-soluble halogen compounds).

Zirconium and hafnium have nearly identical chemical properties, so fractionation observed could serve as an indication for special chemical conditions of a geologic system in forming complexes, and the different diffusion rates of these could eventually lead to a more or less pronounced differentiation. Not until the last few years could the cosmic (chondritic) Zr/Hf ratio be established using a neutron activation technique, which permits determination of both the elements in the very same sample. In most cases it is not possible to determine Hf along with Zr by nondestructive techniques, especially in the very low parts per million range. Therefore, Kumar[17] carried out a radiochemical separation after reactor thermal neutron irradiation. Zirconium and hafnium were separated from each other by repeated alkali fusion and precipitation with hydrophenylarsonic acid. This eliminates problems associated with fractionation of these elements during chemical separation. The technique recently has been applied by Ehmann and Chyi,[18] Chyi and Ehmann,[19] as well as Garg and Ehmann[20] to meteorites and lunar samples, and it has been shown that the lunar Zr/Hf ratio exhibits a narrow range from 36.6 to 51.3, with a mean value of 38, which is close to the meteoritic range of 30 to 35 according to Mason.[21]

It should be noted that all Zr/Hf ratios calculated for individual moon samples using Zr- and Hf-data obtained from different small samples have to be considered with care.

Furthermore, postulation of a Zr^{3+} ion in a multistage lunar crustal evolution model by Garg and Ehmann[20] to interpret low lunar Zr/Hf ratios is highly speculative, not only from the fact that partition coefficient data for Zr and Hf systems as well as quantitative data for conditions necessary for the $Zr^{4+} \rightarrow Zr^{3+}$ reduction are unavailable, but also from the error limits given by the same authors. According to them, error limits increase to 10% in samples containing <100 ppm Zr. Anorthosite 60015 (Zr/Hf ratio ~21) analyzed by the authors contain as little as 0.1 ppm Zr, which is in my opinion not known better than within a factor of 10. Finally, it should be mentioned that the most commonly and routinely reliable method currently in use for the determination of Zr in terrestrial materials is X-ray fluorescence, for which the detection limit is at the parts per million level. For Hf, the most widely applied technique is activation analysis, so the problems discussed are still very real.

Very interesting procedures have been proposed for the separation of the halogens from extraterrestrial samples. From these Cl, Br, and I were determined radiochemically, whereas F usually was determined in conjunction with an ion specific electrode. While neutron activation technique is applied mainly to extraterrestrial rocks, gravimetric and spectrophotometric methods are generally applied for the determination of Cl, Br, and I in terrestrial rocks. Nevertheless, results on extraterrestrial materials are rather sparse, sometimes conflicting, and difficult to interpret. However, the widely varying results either suggest inhomogeneous distribution, which makes sampling a major problem, or indicate experimental error, if we neglect for the moment the possibility of contamination.

Nevertheless, methods only are discussed in this review which enable the determination of most of the halogen elements on the same subsample. Certainly, techniques applied to unrepresentative sample weights will at least establish interelement ratios, viz., Cl/F, Cl/Br, and Br/I as well. Dreibus et al.,[22] however, applied pyrohydrolysis for the quantitative extraction of the halogens using a quartz apparatus. Samples of 50 to 100 mg were pulverized and sieved (100 mesh) prior to the 2-hr irradiation with thermal neutrons. After irradiation the samples were mixed with V_2O_5, heated to 1100°C, and exposed to a stream of water vapor. The extraction time used was 12 min. The volatile halogen compounds were finally absorbed by use of a sodium hydroxide solution and the gamma spectra measured. After the radioactivity measurements, fluorine was determined with an ion-specific electrode. Nevertheless, the method could not be applied with success to moon samples, where the Cl/I ratio is high (> 100) and I contents are in the parts per billion range. The faint gamma lines of the I-128 ($T_{1/2} = 25$ min) disappear in the high background produced by Cl-38 ($T_{1/2} = 37.3$ min) as well as other components volatile under the experimental conditions.

Schaudy[23] proposed solvent extraction of Br and I after irradiation and fusion of the samples with different mixtures, mainly consisting of Na_2CO_3, K_2CO_3, Na_2O_2, and NaOH. In the residual aqueous phase Cl is separated as AgCl. Kiesl et al.[24] have optimized the separation technique with respect to time restrictions as well as detection limits.

Up to 100 mg of sample (minimum sample weight operated by the authors has been approximately 5 mg, a <0.73 μm fraction of moon sample 74,001, as reported by Eugster et al.[25]) was fused with NaOH-Na_2O_2 after irradiation. A 10 to 40 mg carrier of each halogen as well as an I-131 tracer was also added before starting fusion in a zirconium crucible. The fusion cake was dissolved in water, 1 *M* H_2SO_4 was subsequently added and the solution prepared for extraction. First, I was extracted into CCl_4 by addition of $NaNO_2$, followed by extraction of Br into CCl_4 by $KMnO_4$. From the combined organic phases both halogens were back-extracted in a minimum volume by the use of 0.05 *M* H_2SO_4 and H_2SO_3. The gamma spectrum of the aqueous extract was measured. The Cl was separated by AgCl from the diluted aqueous solution obtained after extraction of Br and I. The advantage of this method is: detection limit for Cl being 35 ng, for Br 0.6 ng, and for I 0.1 ng. The disadvantage at the moment is that it is, unfortunately, not possible to determine fluorine simultaneously in the sample.

The lanthanides are a unique group of elements, strongly coherent geochemically and of special interest when dealing with genetic questions of rocks. The distribution of these elements is highly influenced by the geological environment and the crystal structures of the minerals. Therefore, procedures have been developed to separate the REE from the matrix in order to establish their distribution pattern in those cases where the nondestructive activation method fails. This separation step especially is necessary if REE contents in the lowest parts per million or eventually sub-parts per million range are to be expected. Examples include the majority of the ultrabasic rocks and certain groups of meteorites as well as moon materials. Furthermore the distribution of the REE in the individual coexisting rock-forming minerals from different rocks should represent an important genetic indication. Unfortunately, only few data are known in this regard, mainly due to the fact that pure, inclusion free minerals are rare, difficult to separate, available in small quantities only, and last but not least, any separation step is more or less complicated and time consuming. Nevertheless, these operations should also be carried out more frequently in order to verify the REE pattern in these genetically significant materials, since it has been demonstrated clearly by Ringwood[26] that there is a close relation between REE deficient materials and materials in which the lanthanides are enriched.

Taking all these factors into account, a separation step should be economical and quantitative. In this review a separation step is described which separates the REE from the matrix before irradiation, a technique which is not so common in activation analysis because special care has to be directed to avoid contamination effects and fractionation of the elements during the procedure. But on the other hand, the analyst is able to determine each one of the lanthanides despite the fact of half-life and intensity of the gamma line.

The method developed by Klein[27] is based on a fusion of the sample by HF/$HClO_4$ (for silicate matrix), double precipitation of the REE as oxalates with Ca as a carrier and decontamination of the combined oxalates from traces of Mg, Mn, Fe, and Co as well as Sc and Th, and the carrier by simple ion-exchange operations.

The flow sheet of this procedure is given in Figure 1. Results are given in Table 2 where the REE contents of the USGS Standard rock G-2 are compared with those given by Flanagan[28] and Kluger,[29] (the last named author determined the REE by a nondestructive method). It is clearly seen that Pr, Gd, Ho, Er, and Tm are not detected by INAA either for reasons of matrix element interferences or on reasons of background influence.

In order to obtain maximum information on extraterrestrial samples, sophisticated group separations were developed which permitted the full utilization of the desirable features of high-resolution semiconductors without the extra difficulty of separating individual elements. Morrison et al.[30] combined chemical group separation, a high-resolution detector, and a coincidence-anticoincidence system to gain information on 45 elements. Although the method is applicable to a wide variety of rock samples, application to terrestrial rocks is scarce.

The irradiated samples were dissolved with 2 to 3 mℓ H_2SO_4 and 10 to 15 mℓ HF after cooling and addition of carriers. As and Br were trapped by drawing the fumes and gases through concentrated NaOH. Heating and addition of more HF were repeated several times until the samples were completely dissolved. After heating to dryness the residue was dissolved with 30 to 40 mℓ 8 N HCl to a beaker containing 1 to 1.5 g of hydrated antimony pentoxide (HAP). After stirring for 20 to 30 min the HAP was allowed to

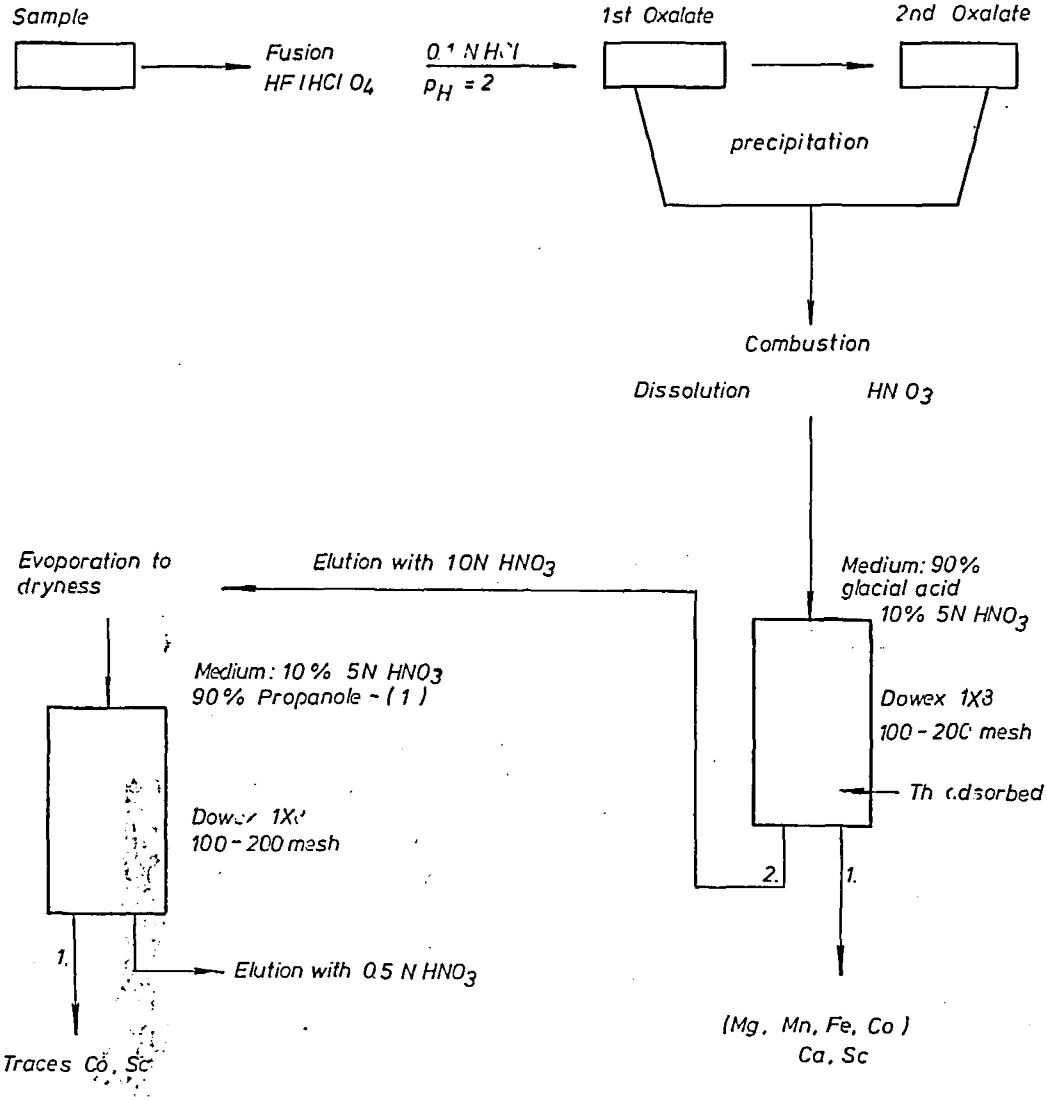

FIGURE 1. Flow-sheet of the preirradiation separation of REE from silicate matrix by Klein.[27]

settle and the supernatant was transformed to a centrifuge tube to separate colloidally suspended HAP. The supernatant was transferred onto a small column of HAP.

The HAP in the beaker was washed several times with small portions of 8 *N* HCl, the solution passed through the centrifuge procedure and onto the HAP column. The HAP contained Na and Ta. The effluent from the HAP column was passed through a column of Dowex 1 × 8 and the column washed several times with small portions of 0.5 *N* HCl. The resin was eluted with small fractions of 0.5 N HCl; the eluate contained Fe, Co, Cu, Ga, W, Mo, and Np. The resin contained the isotopes of Zn, Sb, and Hg.

The 8 *N* HCl eluate from the previous effluent was evaporated to dryness, again dissolved with 8 N HCl and transferred into a separatory funnel and extracted with small portions of TBP. The organic phase comprised Hf, Zr, Sc, and Pa, the aqueous phase K, Rb, Cs, Ba, Cr, Ca, and the REE.

Although the separation procedure is extremely simple, a few complications have to be considered. Ba partly remained on the HAP; even Mo is distributed during the 0.5 *N*

Table 2
REE-CONTENTS OF USGS STANDARD-ROCK GRANITE G-2

	Split-Nr.:30/19 Klein[27]	Split-Nr.30/19[a] Kluger[29]	Flanagan[28]
La	85.0	84.0	96 (r)[b]
Ce	146.0	156.0	150 (m)[c]
Pr	18.0	—	19 (m)
Sm	6.8	6.7	7.3 (a)[d]
Eu	1.23	1.21	1.5 (r)
Gd	5.7	—	5 (m)
Tb	0.56	0.49	0.54 (r)
Dy	2.17	2.5	2.6 (r)
Ho	0.42	—	0.4 (m)
Er	1.37	—	1.3 (m)
Tm	0.25	—	0.3 (m)
Yb	0.75	0.64	0.88 (a)
Lu	0.10	0.089	0.11 (a)

[a] Instrumental neutron activation analysis.
[b] Recommended value.
[c] Magnitude.
[d] Average.

HCl operation of the anion exchange resin. Furthermore, Th was determined via Pa-233 and the isotope was found in at least three groups. The same happened with U; this element was determined via Np-239 which was distributed as well. Moreover Mg, a major constituent in most rocks, had to be determined prior to radiochemical processing by INAA.

To avoid evaluation of gamma-peaks of elements distributed over several fractions during chemical processing, a combination of INAA followed by radiochemical separation has been proposed. In most cases, the determination of elements like Hf, Ta, and Th (Pa) during the INAA-cycle was possible.

Using this combination, it was demonstrated by Kiesl et al.[31] how to determine 27 constituents in lunar samples. INAA comprised two cycles. A very short cycle (irradiation time 20 sec) was used first after which the determinations of Mg, Al, Ca, Ti, Mn, and eventually V were carried out. In a second short cycle (irradiation time 50 min) a spectrum of elements was determined during a cooling period of 26 days. After 1 day of cooling Na, K, and Mn can be determined, after 13 days Sc, Fe, Co, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Th, and Cr, and finally 26 days after irradiation, all the elements of the foregoing group (except La and Sm) were measured in addition to Hf and Ta. Thereafter, samples and standards were irradiated 5 days in the core of the reactor and a simple separation scheme allowed the evaluation of Ca, Rb, Sr, Cs, and U (via Ba-140). All the separation steps are quantitative; therefore microchemical determination of SiO_2 and especially Mg were rendered possible.

After addition of carriers and fusion of the sample with $NaKCO_3$, SiO_2 was determined microchemically by separation as SiO_2, the aqueous solution made 7 *N* HCl and passed through an ion-exchange resin column Lewatit M 5080, Co and Fe were adsorbed and eluted with 3 *N* HCl and 0.5 *N* HCl, respectively. The effluent was evaporated nearly to dryness and the REE, Mn, and Cr were precipitated by NH_3. In the alkaline filtrate Ca was determined and thereafter Sr and Ba precipitated as sulfates. The aqueous solution contained Cs, Rb, and Mg. Amounts of Cs and Rb were evaluated from the solution, and finally Mg was separated as the oxinate and determined microchemically.

A multielement analysis to determine all major and many minor and trace elements has been developed by Wänke et al.[32] for moon samples. Altogether, concentrations of 54 elements were determined via activation methods with only the exceptions being F and P. The procedure comprises four irradiation steps using fast neutron activation, one step using thermal neutron irradiation, and finally thermal neutron activation followed by radiochemical separation.

The first step was a very short cycle (10 sec) with 14 MeV neutrons from a Philips neutron generator PW 5320. Determination of O (via N-16) and Si (via Al-28) was achieved. The second step was a short, fast neutron cycle of 5 min for the determination of Fe (via Mn-56), Mg (via Na-24), and Al (via Na-24).[33] Si was used as an internal standard. The third step was a 1-hr fast neutron irradiation where Sr was determined via Sr-87m. Mn-56 from Fe was used as an internal standard. In the fourth fast neutron cycle (12 hr) determination of Ca (via Ca-47), Ti (via Sc-48), Ni (via Co-57), Y (via Y-88), Zr (via Zr-89, Y-89), Nb (via Nb-92), and Ce (via Ce-139) using Na-24 from Al and Mg as an internal standard was achieved.

In the first reactor neutron activation cycle (6 hr) Na, K, Ca, Ti (via Sc-47), Ca (via Sc-47), Cr, Mn, Ni (via Co-58), Fe, Co, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Yb, Lu, Hf, Ta, Ir, and Th (via Pa-233) were evaluated during a cooling period of 3 weeks in five counting periods.

Finally, after a 6-hr irradiation with reactor neutrons, the samples were decomposed under vacuum with Na_2O_2 and radiochemically processed to determine a spectrum of elements. The detailed description of the separation scheme is given in Rieder and Wänke[34] and Wänke et al.[35]

Carriers of each element to be determined had been added previously, and after several minutes of pumping, Ar and Xe were added as carriers for the extracted rare gases and the sample finally heated by means of high-frequency induction heating. After fusion, Ar and Xe were adsorbed on charcoal at liquid nitrogen temperature and further purified. This procedure offers the possibility of determining simultaneously the content of U via Xe-133 and of Ca via Ar-37.

The melt was treated with H_2O, unsoluble parts centrifuged and dissolved in HNO_3. The solutions were combined and hydroxides precipitated with NaOH at pH 8. The supernatant was adjusted to pH 11 by NaOH and the hydroxides centrifuged off. To the supernatant, Na_2CO_3 was added to precipitate the carbonates of Cu, Sr, and Ba.

Finally, the filtered solution was adjusted to pH 2 with HCl, and K, Rb, and Cs precipitated with tetraphenylboron. From the different hydroxide precipitations the elements Au, In, Ga, Ge, As, Pa, REE, Pd, Cu, W, Co, and Ir were separated by very time-consuming procedures of precipitations and extractions. Due to the distribution of many of the elements on several fractions, yield determinations after counting were necessary. Yields were close to 100% for only Ar and Xe, about 90% for K, Ga, and Au, and between 50 to 80% for the remaining elements. Nevertheless, the method described is an outstanding example of a working procedure based mainly on activation analysis. It should be mentioned that for a number of elements like Ga, As, Hf, and W the authors reported the first results on anorthositic rocks.

To discuss neutron activation with respect to efficiency and reliability of results, I have chosen results of soil sample 10084 (Tables 3, 4, and 5) for several reasons. It is certainly a homogeneous and representative sample down to the tens of milligram range. Work on this lunar soil sample started nearly simultaneously in the various laboratories, and moreover independently. REE distribution was almost unknown until this moment.

It is clearly seen that classical chemical analysis dominates NAA and even other instrumental methods. Although representative results are obtained by classical

Table 3
COMPOSITION OF LUNAR SOIL SAMPLE 10084 AS OBTAINED BY NAA.[a]

Major and minor elements (Weight—%)

	(a)	(b)	(c)	(d)	(e)	(f)
Si	—	—	17.5	19.7	19.75	19.74
Al	7.3	—	7.1	6.9	7.28	7.32
Ti	4.1	4.4	3.9	4.3	4.40	4.52
Fe	12.5	14.0	12.0	12.0	12.45	12.28
Mg	4.6	—	4.8	4.8	4.78	4.81
Ca	9.6	—	7.4	8.1	8.58	8.55
Na	0.33	0.3	0.31	0.31	0.311[b]	0.32
K	0.11	0.1	0.09	0.109	0.108[b]	0.108
Mn	0.16	0.125	0.16	0.156	0.154	0.155
Cr	0.20	0.22	0.178	0.183	0.225[b]	0.188

Note: (a) Morrison et al.[36] Sample weight 100 mg.
(b) Turekian and Kharkan.[37] Sample weight 20 mg.
(c) Schmitt et al.[38] Sample weight 100 mg.
(d) Wänke et al.[39] Sample weight 100 mg.
(e) Maxwell et al.[40] Sample weight 1 g (?). Classical method.
(f) Wiik and Ojanpera.[41] Sample weight 1 g. Classical method.

[a] Included classical chemical analysis.
[b] Results obtained by AAS.

Table 4
COMPOSITION OF LUNAR SOIL SAMPLE 10084 AS OBTAINED BY NAA.
TRACE ELEMENTS (ppm)

	(a)	(b)	(d)	(g)
Sc	60.0	80.0	61.0	n.d.
Co	40.0	33.0	27.2	26.8
Cu	9.8	38.0	8.2	7.75
Zn	22.0	n.d.	n.d.	21.0
Ga	4.6	n.d.	4.9	5.24
Rb	4.4	n.d.	3.0	3.09
Cs	0.2	n.d.	0.12	0.094
Hf	9.0	11.0	15.6	n.d.
Ta	1.3	1.8	1.3	n.d.
Th	2.3	n.d.	1.25	n.d.
U	0.48	0.33	0.35	n.d.

Note: (a) Morrison et al.[36]
(b) Turekian and Kharkar.[37]
(d) Wänke et al.[39]
(g) Keays et al.[42] Sample weight 100 mg.
n.d. = Not detected.

methods, the difference between those of Maxwell et al.[40] and Wiik and Ojanpera[41] is insignificant, the spectrum of elements to be determined is considerably restricted. For reasons mentioned previously, geochemical interpretations get more and more problematic as the sample weights are reduced. Therefore, work on small samples should

Table 5
REE-COMPOSITION OF LUNAR SOIL SAMPLE 10084 AS OBTAINED BY NAA AND SID-MS. (CONTENTS IN ppm)

	(a)	(b)	(d)	(h)	(i)	(j)
La	11.0	20.0	15.0	16.3	—	19.0*
Ce	34.0	79.0	63.0	47.6	46.1	46.0
Pr	8.7	n.d.	5.3	—	—	—
Nd	43.0	n.d.	47.0	36.8	40.4	37.0
Sm	14.0	8.7	7.6	13.1	13.9	13.0
Eu	1.6	2.0	1.67	1.77	1.77	1.8
Gd	17.0	n.d.	18.0	17.2	—	—
Tb	3.5	n.d.	2.8	—	—	4.0*
Dy	30.0	17.0	17.0	19.7	19.5	23.0*
Ho	7.0	n.d.	4.6	—	—	5.0*
Er	19.0	n.d.	9.5	21.1	11.7	—
Tm	1.2	n.d.	n.d.	—	—	—
Yb	15.0	9.5	8.3	11.5	10.6	12.0*
Lu	1.5	1.3	1.30	1.58	—	1.5

Note: (a) Morrison et al.[36] NAA.
(b) Turekian and Kharkar.[37] NAA.
(d) Wänke et al.[39] NAA.
(h) Gast et al.[43] Sample weight 200 to 300 mg. SID-MS.
(i) Philpotts and Schnetzler.[44] No sample weight reported. SID-MS.
(j) Smales et al.[45] No sample weight reported. SID-MS.
* = Result obtained by neutron activation.

be achieved rather for mineral separates or fractions from lunar soil and rocks in comparison with a representative analysis, which will enable the analyst to discuss element distributions more correctly.

In Table 4, variations of trace elements of the same soil sample are given. Deviations in the case of Sc, Co, Cu, Hf, and Cs up to a factor of $\sim$ 4 are observed. Finally, in Table 5, variations in REE contents are given. From this table it is seen that the most reliable results are obtained by the stable isotope dilution method on sample weights of 200 to 400 mg. Figure 2 shows a plot of these results with respect to the chondritic norm values, which in fact, serve as an indication for differentiation processes.

Since accuracy by neutron activation is reported in the range of 5 to 10% and accuracy by SID-MS on the order of 2 to 5%, deviations from the expected distribution curve results mainly due to the fact that accuracy by neutron activation is largely based upon calculation of the net-peak area, ignoring the contribution of the background. This is especially of importance if INAA results are calculated. From the table and the figure it is seen clearly that SID-MS will approximate best the normally expected smooth REE distribution curves for moon samples. There is only one erroneous number in Gast's results, namely for Er (21.1 ppm, norm-value $\sim$ 100). If we pay attention to the results of Philpotts we see that for Er the expected value (11.7 ppm, norm value $\sim$56) appears.

As in the case of interelement ratios, inhomogeneity of the sample would lead to a shift of the curves along the ordinate. Since there is no indication for a shift as seen from Figure 2, moon sample 10084 is expected to be homogeneous down to the milligram range, concerning at least the REE distribution pattern.

In the past few years, as interest on moon samples decreased to some extent, an increasing trend toward application of radiochemistry to terrestrial samples was

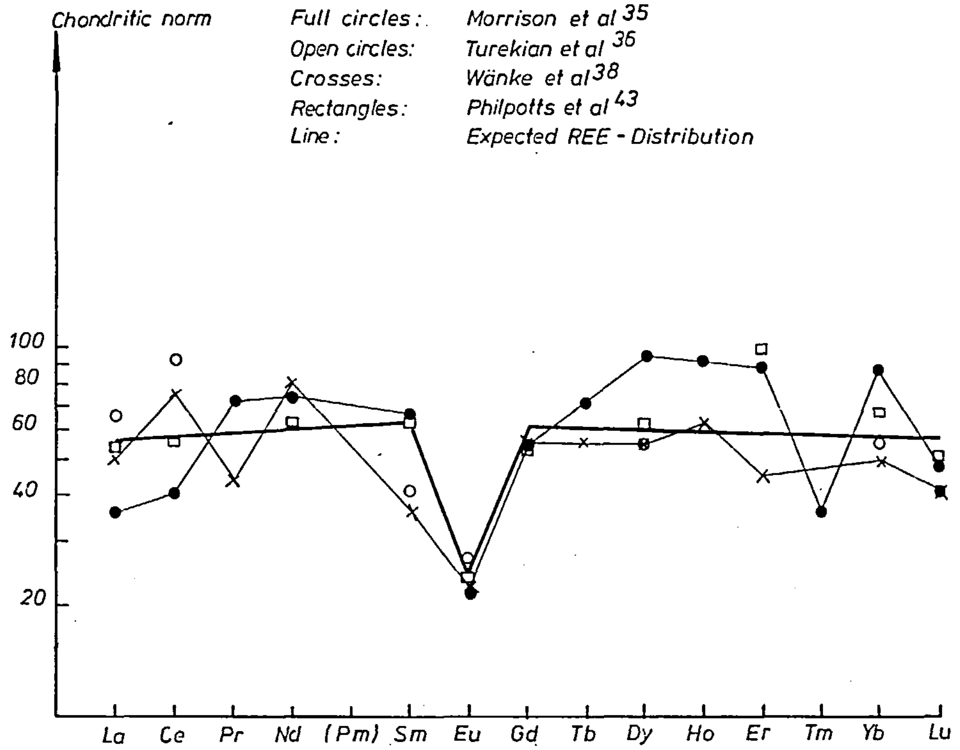

FIGURE 2. REE—Distribution in lunar soil 10084.

observed. The field of geothermal energy research especially has been stimulated by Blommaert et al.[46] with respect to evaluation of trace and ultratrace data. Sampling and storage problems, risks of contamination, and the necessity to invoke extraordinary analytical techniques render interpretation of the data more difficult. On the other hand, trace element data might be useful to demonstrate mixing of geothermal with surface waters, to estimate the total heat flux through a geothermal reservoir, etc. The authors describe a simple multielement preconcentration procedure for dissolved metals in natural waters through the use of PAN 1-(2-pyridilazo)-2-naphthol as a co-crystallization agent. The procedure is based on the following steps. To a water sample aliquot at pH 9 of 0.5 to 2.5ℓ, some milliliters of a 0.2% solution of PAN in ethanol was added. Subsequently the sample was heated to 70 to 80°C for 10 min. During cooling PAN crystallized out, collecting many ions from the solution, such as Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and REE. Recoveries are above 90%. For Sc, Co, Zr, Fe, Ag, Cd, Sn, In, Hf, Hg, U, and Th recoveries reported are above 70%. It is of interest that results are essentially independent of sample volume as well as major ion content of at least up to 30% NaCl, 1000 ppm Mg^{2+}, and 500 ppm Ca^{2+}. Even in sulfide medium, simulating sulfide geothermal waters, no significant different collection yields were observed.

This section should not be ended without reference to outstanding reviews in the field of neutron activation analysis of geological materials written by Gijbels and Hertogen,[47] Gijbels,[48] and Laul.[49]

B. X-Ray Analysis

1. X-Ray Fluorescence Analysis

This method is concerned with the analysis of electromagnetic radiation emitted by the elements. The term "fluorescent" is used to denote a particular method of exciting the elements, viz., by irradiation with primary X-rays, generally from an X-ray tube. The characteristic X-rays emitted by the elements are then analyzed by methods analogous to those used in optical emission spectrography. X-ray work is generally limited to wavelengths between 0.3 and 5 Å.

X-ray fluorescence analysis (XFA) of terrestrial and extraterrestrial materials has become a widely adopted method during the past 2 decades. Recent developments in the field of X-ray fluorescence apparatus promised a certain progress in light element analysis and routine trace element analysis. The technique breaks down into excitation, dispersion, and data manipulation. These three main areas have been discussed extensively by Macdonald.[50,51]

Soon after the growth period of X-ray spectrometry, where work was concentrated on improving the hardware and the instrumental technique, it was realized that sample preparation methods had to be well controlled if reliable and accurate results were to be obtained. As a comparative method it follows that unknown samples and standards must be made truly comparable in essential respects: in their surfaces, in particle size if they are powders, in degree of heterogeneity, and in the way they are presented to the X-ray beam. In most cases the samples must therefore be prepared for spectrography.

To overcome these problems, samples are usually transformed into a glass by fusion with lithium tetraborate. Although dilution reduces the counting-signal, matrix effects become constant and a simple relationship will exist between fluorescent intensity and concentration. Dilution of the sample, on the other hand, affects negatively the determination of trace elements by the method. Various methods will be discussed in this chapter to permit the determination of trace elements down to the sub-parts per million range. Usually the expected limits of detection for most elements of $Z \geqslant 15$, in the case of favorable elemental conditions, undiluted samples and short counting times are in the lower parts per million range.

The most important paper on an accurate X-ray fluorescence determination of main and minor constituents of a wide range of geological samples is that by Norrish and Hutton.[52] This work is also the basic one for development of procedures applied to extraterrestrial samples. More recently the problems of the quantitative XFA-method have been discussed by Stern.[53]

Samples for analysis are prepared by mixing of 1.5 g of borate glass, 0.02 g sodium nitrate, and 0.28 g of powdered rock. Borate glass is prepared by heating a mixture of 38.0 g lithium tetraborate (anhydrous), 29.6 g lithium carbonate, and 13.2 g lanthanum oxide; the latter is essential to increase absorption and thus reduces matrix effects. Sodium nitrate is added to ensure oxidizing conditions, and although it is unnecessary in most cases, it is always added to standardize the technique. This mixture is heated to 1000°C for 5 to 10 min until all the sample has dissolved. Finally the melt is poured on a graphite disc, kept hot at about 220°C and cooled slowly for a few minutes. Although the sample preparation method described is simple and quick, the success of the analysis depends on various details. (See Norrish and Hutton.[52])

Stern[53] fuses 150 mg of a previously ignited pulverized sample with 2.35 g lithium tetraborate in a Pt-Au-crucible at 1070°C for 5 min. The cooled mass is then poured in a Pt-Au-crucible and heated in a conductive furnace at 1100°C for 4 min. Cooling of the glass is a critical procedure. Application to lunar samples has been carried out, e.g., by Cuttitta et al.[54] and Duncan et al.[55] Cuttitta et al. applied a simple fusion with no heavy absorber to 60 mg of moon samples. The sample was fused with 940 mg lithium tetraborate at 1100°C for 15 min. After cooling, the fused bead was brought to 1200 mg with powdered cellulose and then was ground to less than 350 mesh. Duncan et al. used a technique described by Willis et al.,[56] which is more or less a modified version of that by Norrish et al.[52]

Concerning trace elements, two methods for the sample preparation are given by Stern.[57] In the first method, 800 mg of the finely ground sample is mixed with five drops polymer (16% Elvacite in toluol), dried and subsequently pressed into a constant volume, giving an average density of 2.3 g/cm^{-3}. It should be noted that varying granulometries as a result of different mineral fragility remain a cause of possible analytical error.

In the second preparation technique, 150 mg of ignited powder is carefully mixed in an agate mortar with 2.35 g dried lithium tetraborate, filled in a Pt-Au cup, and melted for 30 min in a muffle furnace at 1070°C. Samples and flux are stored at 105°C in a heating oven, thus avoiding adsorption of moisture.

Depending on analytical demands, a simple sample preparation with polymers enables sufficiently accurate determinations in the case of low concentration levels from 10 to 1000 ppm. For higher concentrations, dilution techniques or absorption corrections become necessary for a number of elements.

Although XFA is a widely applied technique for the determination of major and minor components in geosciences, it fails in the trace-element region. In common silicate rocks the number of trace elements that can be estimated is very limited and, moreover, reduced to those elements not necessarily needed for genetic interpretations. Therefore, chemists have proposed different procedures for preliminary chemical enrichments and separations of the trace elements from the original sample in order to enhance both sensitivity and accuracy.

Roelandts[58] studied ion exchange procedures for enrichment and separation of the REE from apatite. About 0.5 g of the sample were weighed and dissolved in 7 N HNO_3. After dissolution, the solution was evaporated to dryness, taken up in a mixture of 5% 7 N HNO_3 to 95% CH_3OH and transferred to a screw-capped polyethylene bottle containing 0.5 g of accurately weighed amounts of dry anionic resin in the nitrate form. The batch equilibration process provides some advantages over the column technique, one of which is homogeneous distribution of the ion of interest on the resin. The support for the resin beads used in the XRF analysis consisted of a cellulose disk. Although agreement between results obtained by neutron activation analysis and XRF analysis of two phosphate samples is reasonably good, limits of determination for the elements investigated (La, Ce, Pr, Nd) are poor, viz., 3 to 10 ppm. As the author stated, these detection limits are not definitive and could be lowered by using longer counting periods. Unfortunately the investigator did not extend research work to the heavy REE, so it is not possible to obtain a distribution pattern, which would be essential for discussion of differentiation processes, genetic questions, etc.

Blommaert et al.[46] discussed XRF analysis of preconcentrated trace elements from natural water. The method is very similar to that described earlier. With PAN, preconcentration factors up to 200,000 can be achieved. The PAN precipitate is loaded on a filter, dried, and exposed to the X-rays for 1,000 to 10,000 sec. The authors discuss the method extensively and conclude that XRF would be ineffective after PAN preconcentration in the case of bicarbonate waters. Ni is lost in any case.

A very interesting application of XRF is described by Pietiläinen et al.[59] The authors described a multielement analysis of phytoplankton by the method. The water samples were filtered over a membrane filter with a 0.45-μm pore size and a diameter of 47 or 50 mm. A broad spectrum of elements, Ti, Mn, Ni, As, Rb, K, V, Fe, Cu, Sc, Sr, Ca, Cr, Co, Zn, Pb, Cl, and Br could be detected. Detection limits are in the low parts per million and in a few cases in the sub-parts per million range.

Finally, I would like to discuss another attempt to extend XRF to the trace element region. This has been carried out by Barrios et al.[60] The authors carried out determination of uranium in aqueous solution by XRF in complex mineral matrix. For this purpose a solvent extraction method was found using TOPO in benzene as a complexing agent and solutions of tartaric acid, sodium fluoride, EDTA, and HDTA as masking agents. The organic phase was finally exposed to the X-rays. Agreement between this technique and NAA is again satisfactory; the method works down to a level of 3 ppm, which is well above the limits of detection for INAA, even so for a more or less complex matrix. So the advantages are to be found in short analysis time, low cost, good accuracy, and precision.

From these considerations it should be clear that XRF analysis is a good tool for the determination of major and minor elements and obviously a limited number of trace elements in geosciences, viz., V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Ba, and Pb. It may be applied to a certain range of trace elements after their preconcentration, but is not very suitable for single trace element determinations after chemical processing. In these cases a selective extraction method followed by spectrophotometric determination seems to be more convenient.

2. *Electron Microprobe Analysis*

This method is not principally different from XRF analysis concerning the electromagnetic signal evaluated for analytical purposes. The elements of the sample, however, are excited by electrons. As the excited volume in the sample produced by the focused electron beam is about 1 μm^3 and the "sphere of influence" is dependent on the atomic numbers of the constituents of the sample as well as the energy of the incident electron beam, quantitative calculations are extensive and based on sophisticated views of the interaction between electrons and matter. Numerous publications deal with these viewpoints and need not be stressed again in this paper. In any case, the method became an indispensable tool to petrologists in obtaining accurate phase composition data.

Since application to geosciences is so useful, it is really hard to select certain special fields for a more detailed discussion. Nevertheless, two topics largely disregarded in most review papers will be discussed. One comprises investigations of oxidation states of elements in geologic samples; the other, sample fusion techniques for whole rock analysis with the electron microprobe.

Microprobe analysis is, apart from the latter application, a nondestructive method. Sample preparation comprises in most cases physical processes, viz., polishing and coating with a conductive layer in the case of nonconducting materials.

Before beginning the selected topics, I should try to present at least a general overview of the literature. More recently, very valuable reviews have been given by Long,[61] Malissa,[62] and Macdonald.[63] The broad field of application is best demonstrated by a volume of the *Basaltic Volcanism Study Project*[64] which deals with basaltic volcanism on the terrestrial planets, comprising application of the method to terrestrial and extraterrestrial materials as well. Beyond that, most information on new minerals detected by the method is found in periodicals of geosciences.

Because many elements occur in two or more oxidation states, oxidation and reduction are geochemically important processes. Iron is found in nature in the oxidation states 0, 2, and 3. The meteorites represent a considerably lower oxidation state than do terrestrial rocks. Lunar mare basalts crystallized under conditions of lower oxygen fugacities than occur in extrusive equivalents on earth. Thus reduced oxidation states of Ti and Cr have been detected in certain lunar materials.

In the early 1970s, Albee and Chodos,[65] Pavićević,[66,67] and Smith and O'Nions[68] demonstrated that electron microprobe investigations can provide information on the oxidation states of the third transition elements in many rock-forming minerals. Pavićević et al.,[69] however, applied the technique on a quantitative basis and restricted measurements to members of simple binary systems like the ilmenite-hematite or the ulvospinel-magnetite series. In such simple binary systems, the L-emission spectra are influenced mainly by the oxidation state of the transition element under investigation.

The authors describe the difficulties in obtaining quantitative statements. Sung et al.[70] reported first quantitative results on the distribution of Ti^{3+} and Ti^{4+} in lunar pyroxenes using a combination of electron microprobe and electronic spectral measurements. The authors used polished sections of the samples, 100 μm thick, for both microprobe and absorption spectral measurements in the visible and near infrared region. The results show that appreciable, though variable, percentages of Ti^{3+}-ions occur in lunar pyroxenes. Thus, about 30 to 40% of the titanium in the lunar pyroxenes occurs in the trivalent state.

In meteoritic material Dowty and Clark[71,72] derived the chemical formula of an iron-free titanium fassaite to be $Ca_{1.01}\ Mg_{0.38}\ Ti^{3+}_{0.34}\ Ti^{4+}_{0.14}\ Al_{0.87}\ Si_{1.26}\ O_6$, indicating that about 71% of the titanium occurs as Ti^{3+}-ions.

Although these studies would be of significance with respect to crystallization conditions within planetary bodies, Sung et al.[70] suggested that factors other than oxygen fugacity control the Ti^{3+}/Ti^{4+} ratios in lunar materials, but few contributions deal with this matter. This may be due to the fact that these investigations are really quite labor intensive and theoretically complicated.

Since 1964, when the paper of Arrhenius et al.[73] appeared, major element whole rock analyses have been attempted. Sample preparation techniques reported are very similar to those previously described in the chapter dealing with X-ray fluorescence. Many investigators used fusion of rock powder with a flux and fusion without flux. Moreover, broad beam electron microprobe analysis has also been applied to obtain bulk rock chemistry.

Gulson and Lovering[74] prepared glass discs by fusing the rock powders with a borate flux. On the same basis with X-ray fluorescence and wet chemical analyses the authors concluded that electron microprobe analyses provide a tool for the fairly rapid and accurate bulk analysis of rocks. The composition of the mixture used by Gulson and Lovering was: 39.6% $Li_2B_4O_7$, 30.9% Li_2CO_3, 13.8% La_2O_3, and 15.7% rock powder. However, Reed[75] found that the lanthanum used in lithium tatraborate fusions for X-ray fluorescence analysis should preferably be omitted in the preparation of glasses for electron microprobe analysis.

A direct fusion technique was applied by Rucklidge et al.[76] to small quantities of material and obviously developed for the analyses of lunar samples. Graphite crucibles were used as sample containers for rocks and the fusion was carried out in a platinum wound quench furnace. Hydrogen was passed through the furnace to prevent excessive oxidation of the graphite. Between 0.05 and 0.1 g of rock powder was used for the fusion, and at the end of each run the sample was quenched by dropping the container into distilled water. Temperatures approximately 100°C above the liquidus for a duration of 10 to 15 min were found to be adequate to produce satisfactory glasses. The authors discuss the limitations imposed by the fusion process. Rocks with very high liquidus temperatures such as dunites and peridotites or those containing small amounts of very refractory minerals such as corundum or spinel would not be completely fusible. Further limitations arise because the fusion process drives off volatile constituents such as H_2O and CO_2, their removal may affect the fusion and, even if it does not, the volatile free analyses might be of limited use. Furthermore, the authors reported certain difficulties with the granites analyzed, as the liquids are much more viscous and a much longer run is required to produce homogeneous glasses.

A similar technique has been proposed by Brown[77] in which the sample is melted on a strip heater housed in a pressurized aluminum canister equipped with electrical terminals, gas fittings, and a pressure gauge. A quartz window for sample viewing and temperature calibration with optical pyrometer is located on top. Approximately 20 mg of rock powder, about 50 μm grain size, is placed on a molybdenum heater strip. The canister is first pressurized to 60 lb/in.^{2} with argon and flushed several times while maintaining the pressure. The molybdenum strip is then heated to 900°C for 15 sec to drive off H_2O and CO_2 from the sample. The temperature is then increased sufficiently above the rock liquidus to insure complete melting of the sample. Melting takes approximately 5 sec; an additional 15 to 20 sec at the run temperature helps promote mixing of the melts. For andesites and basalts, temperatures vary from 1450 to 1650°C; for syenites, granodiorites, and granites, 1650 to 2000°C is necessary.

With the exception of Na_2O in standard rock G2, errors for the major elements generally are less than 5% relative. Nevertheless, the conclusion of the author is valid that this method is particularly attractive where sample size is small, large number of analyses are required, or the electron microprobe is the principal analytical instrument available.

Broad beam electron microprobe analysis also has been used to obtain bulk rock chemistry. Again, this method has been developed for the analyses of lunar rocks. The method is discussed by Prinz et al.[78] and applied to moon samples by Keil et al.[79] by moving the sample under a broad (~200 μm diameter) beam until it was completely covered. As discussed by Dowty et al.[80] a large degree of uncertainity is associated with the technique. As has been discussed by the latter authors, a systematic bias is present for certain elements. Aluminum and calcium values appear to be somewhat higher; and iron, magnesium, and titanium values appear to be somewhat lower than those obtained by wet chemical, X-ray fluorescence, neutron activation, and atomic absorption techniques. According to the authors, possible causes of such biases would seem to be very limited. Different plucking and/or cracking of minerals in thin-section preparation, and avoidance by the microprobe operator of severely plucked or cracked areas in the sections during analysis are taken into consideration. Several correction factors have been proposed.

From these difficulties it seems clear that electron probe microanalysis for determination of the bulk chemistry should be applied to very special cases because of the difficulties discussed before and the possibilities of a chemical change brought about by alkali loss, which would be much more significant than difficulties with volatile components, such as H_2O and CO_2, and the unknown extent of interaction of the melt with the materials of the containers during the fusion process.

C. Spectrochemical Analysis

1. Arc and Spark Emission Spectrophotometric Analysis

Optical emission spectroscopy is the oldest instrumental method known for analysis of terrestrial matter. In principle, a minute part of the sample is vaporized and excited to the point of light emission. This may be done by means of a DC or AC arc, a spark, a discharge under reduced pressure, i.e., glow discharge lamps and hollow cathodes, laser, flame (see section on flame emission spectroscopy, FES) or a plasma source for solution analysis (see section on inductively coupled plasma atomic emission spectroscopy ICP-AES). An inventory of the emission spectroscopic instrumentation has been given recently by Broekaert.[81]

Since arc and spark sources remain important for trace survey analysis of solid materials in earth sciences, I shall consider these methods exclusively. It should be mentioned however, that no single excitation source is best for all applications. The analyst should have available a wide variety of sources which can be selected in accordance with the analytical requirements. Factors which influence the type of excitation required include concentration of the elements being determined, the vapor pressures or volatilities of these elements and the matrix, the excitation potentials of the spectrum lines that must be used, and the physical condition of the sample. For solid samples, generally available in rock analysis, arc excitation is more sensitive while spark excitation is more stable.

Before proceeding to a more detailed discussion of sample preparation for emission spectroscopy, it should be noted that excellent review articles have been published within the past years. One of the most complete is that of Barnes;[82] a more recent one is by Boyko et al.[83]

The optical spectrograph is one of the more widely used instruments in geochemical investigations. About 20 years ago it was generally believed that the method also would become a tool in the field of cosmochemistry (Ahrens,[84] Taylor and Ahrens.[85]). The development in the analytical instrumental field has shown that there are more suitable methods available for the analysis of extraterrestrial matter, although the ultimate advantage of emission spectroscopy discussed in this chapter is speed of analysis, a factor which should not be completely disregarded these days. The main problem, however, is the preparation of the sample, which is really troublesome in those cases where sample material is restricted. Therefore, application to extraterrestrial matter is restricted to a certain period up to the early 1970s.

One of the very few applications to moon samples is that by Annell and Helz.[86] These authors described in detail the preparation of the samples for emission spectrographic determination of some trace elements in lunar rock samples. Each sample was first crushed and pulverized. Furthermore, the samples were ground to an impalpable powder with an agate mortar and pestle. A 200 mg portion of the finely ground sample was subsequently mixed with 50 mg of graphite powder. This mixture again was ground in an agate mortar and stored in polyethylene capsules. For the investigations, three modifications of DC arc emission spectrography were used. First, a sample mixed with graphite was excited by an arc at 15 A DC in air with a 3.4-m Ebert spectrograph; 38 elements were determined. Second, a sample mixed with Na_2CO_3 buffer was excited in an argon atmosphere with a 3-m Eagle spectrograph. Nine volatile elements were determined. Third, a sample mixed with a K_2CO_3 buffer was excited in an arc in air with a 3-m Eagle spectrograph to determine three alkaline elements. In a table given by the authors it is shown that detection limits in favorable cases are in the low parts per million range, for Ag and Au in the order of 0.2, whereas detection limits for geochemically important elements such as the Rare Earth Elements, Th, U, and others are in the order of hundreds of parts per million.

Table 6 contains approximate detection limits using DC arc excitation for those elements where detection limit is equal to or less than 10 ppm. Also given are the crustal and chondritic abundances in parts per million. Detection limits usually depend on various factors and are subject to extension by factors of 10 to 100, so limits given should not be regarded as fixed, but dependent on the analytical conditions.

Elements to be determined vary from one rock type to another and depend on geochemical distribution as well as spectrographic sensitivity. Still valid is an excellent paper by Ahrens,[88] giving a list of elements to be expected from a standard spectrochemical analysis of common silicate rocks. More recently, a review of developments of optical emission spectroscopy with respect to the analysis of geological materials has been published by Schroll.[89]

A comprehensive study to establish the accuracy of analytical results using selected spectrographic procedures for simultaneous trace analysis of geological materials has been published by Maessen et al.[90] The arcing conditions tested were chosen so as to provide a good compromise with respect to detection limits, precision of line intensities and intensity ratios, and speed of analysis.

Six alternative procedures were employed. They are subdivided into two main categories: (1) those in which samples and standards were fused prior to arcing, and (2) those in which samples and standards were arced in unfused form. In each category, a further differentiation is made according to the reference elements (internal standards) incorporated into the procedure.

In the fusion procedure the beads of standards and samples were prepared by mixing

Table 6
DETECTION LIMITS USING DC ARC EXCITATION COMPARED WITH CRUSTAL AND CHONDRITIC ABUNDANCES[a]

Element	Detection limit		Crustal and chondritic abundance[85,87]	
	Taylor et al.[85]	Annell et al.[86]		
Ag	0.5	0.2	0.08	0.1
Al	2.0	n.d.	8.13%	1.1%
Au	10.0	0.2	0.002	0.2
B	10.0	10.0	3.0	1.0
Ba	3.0	n.d.	1,000.0	4.0
Be	10.0	n.d.	2.0	0.045
Bi	10.0	1.0	0.2	0.01
Ca	1.0	n.d.	3.63%	1.2%
Cd	10.0	8.0	0.15	0.05
Co	5.0	n.d.	20.0	500—900.0
Cr	1.0	n.d.	100.0	3,600.0
Cs	2.0	1.0	5.0	0.1
Cu	0.5	n.d.	55.0	90.0
Dy	10.0	n.d.	5.0	0.3
Er	10.0	n.d.	3.0	0.2
Eu	10.0	n.d.	1.0	0.07
Fe	5.0	n.d.	5.04	21.8—27.6
Ga	3.0	n.d.	19.0	5.0
Ge	5.0	1.0	1.1	10.0
In	1.0	1.0	0.11	0.01
K	2.0	n.d.	2.592	850.0
La	10.0	n.d.	18.0	0.3
Li	0.5	n.d.	32.0	1.8
Lu	10.0	n.d.	0.8	0.03
Mg	1.0	n.d.	2.09%	14.8%
Mn	5.0	n.d.	1,000.0	2,350.0
Mo	5.0	2.0	1.0	1.5
Na	0.5	n.d.	2.38%	0.6%
Nd	10.0	100.0	24.0	0.6
Ni	5.0	n.d.	35.0	1.10—1.91%
Pb	2.0	1.0	15.0	0.3
Pd	10.0	n.d.	0.004	1.0
Pr	10.0	n.d.	5.5	0.1
Rb	1.0	n.d.	115.0	3.0
Rh	10.0	n.d.	0.001	0.2
Ru	10.0	n.d.	0.001	1.0
Sc	2.0	n.d.	20.0	8.0
Si	10.0	n.d.	27.7%	18.0%
Sn	10.0	10.0	2.0	0.7
Sr	5.0	n.d.	450.0	10.0
Tb	10.0	n.d.	0.9	0.05
Ti	10.0	n.d.	4,400.0	650.0
Tl	1.0	1.0	1.3	0.01
V	5.0	n.d.	110.0	65.0
Y	10.0	n.d.	28.0	2.0
Yb	10.0	n.d.	3.0	0.2
Zr	10.0	n.d.	156.0	6.0

Note: n.d. = Not determined.

[a] ppm, except where indicated in % weight.

the synthetic matrix or the sample with $LiBO_2$ in a 1:1 ratio. The mixture was heated under conditions that evaporation losses of trace elements were negligible. The loss in weight due to CO_2 evolution was determined for each bead, and the amount of powdered bead loaded into an electrode was correspondingly adapted so that an electrode always contained the same amount of initial substances. The bead powder was mixed with such an amount of a 1:14 LiF-graphite mixture that a total charge of 40.0 mg was ensured. Bead powder loads were in between 19.0 to 19.9 mg. The initial substances of the standards were 8.0 mg of a 7:2 SiO_2-$CaCO_3$ mixture, 2.0 mg SiO_2 to which the analysis and reference elements were added as oxides, as well as 10.0 mg $LiBO_2$. The initial substances of the samples were 8.0 mg rock sample, 2.0 mg SiO_2 to which the reference elements were added, as well as 10.0 mg $LiBO_2$.

The electrode loads for the unfused samples consisted of 8.0 mg rock sample, 2.0 mg SiO_2 to which the reference elements were added, 7.4 mg Li_2CO_3, 1.3 mg LiF, and 16.3 mg graphite, a total of 35.0 mg. The standards were prepared by 8.0 mg of a 7:2 SiO_2-$CaCO_3$ mixture, 2.0 mg SiO_2 to which the analysis and reference elements were added, 7.4 mg Li_2CO_3, 1.3 mg LiF, and 16.3 mg graphite.

Experimental conditions were a gas-stabilized 10 A DC arc operating with a double-flow device using a 1:9 O_2:Ar mixture as the stabilizing gas and pure argon as the sheathing gas, photographic photometry with emulsion calibration, background correction, and automatic data processing.

From these investigations the authors were able to show that the majority of the analytical results identified as "inaccurate" were results that were too high. Interestingly, the magnitude of the deviation of a result from the "true" value was extremely pronounced with respect to moderate volatile elements. Fusion of both standards and samples prior to arcing substantially improved the accuracy attained for the moderate volatile elements and left the satisfactory accuracy reached with a nonfusion procedure for the elements of high and low volatility intact.

As is seen from these considerations, arc emission spectrographic analysis may also be very time consuming if special care is directed to sample preparation, which on the other hand will result in reliable results. Currently, an increasing number of very different kinds of substances are being analyzed in an efficient manner, not only in earth sciences. Therefore, promptness is often more important than high accuracy and precision. The technique of atomic emission has been investigated by Ehrlich et al.[91] with regard to its universality; powdered samples are simply mixed with Li_2CO_3 and graphite powder (1:4:20) and burnt to completion in a DC arc.

Finally, the method should be discussed with respect to the REE determination. As seen from Table 6, detection limits of the REE should be less than 10 ppm in very favorable cases only. Separation of these elements as a group ordinarily should precede the analysis. This separation not only allows for preconcentration of the REE so that lower detection limits are possible, but also simplifies the analytical problem when geological samples of widely varying composition are encountered.

As described in previous sections nearly every type of separation of the REE from a matrix can be found in the literature. Ion exchange, extraction procedures, and precipitation steps are suggested in most cases. One of the most interesting refinements, however, is to concentrate the REE with the aid of a carrier. Yttrium has been proposed by Hettel and Fassel,[92] because its ionic radius is about the same as for Dy^{3+}, so that its chemical properties closely resemble those of the whole group. Furthermore, the emission spectrum of Y is relatively simple; hence line interferences rarely arise from the carrier.

After separation of the REE as a group, the spectral analysis can be accomplished with

Table 7
DETECTION LIMITS AS WELL AS MINIMUM CONCENTRATION TO BE ESTIMATED QUANTITATIVELY BY THREE-ELECTRODE DC ARGON PLASMA FOR SELECTED ELEMENTS. (SPECTRA SPAN III DATA)

Element	Detection limit (µg/mℓ)	Quantitative (µg/mℓ)	Element	Detection limit (µg/mℓ)	Quantitative (µg/mℓ)
Li	0.001	0.005	Cu	0.001	0.005
Be	0.001	0.005	Ga	0.025	0.125
B	0.003	0.015	As	0.03	0.15
Na	0.001	0.005	Se	0.03	0.15
Mg	0.0001	0.0005	Rb	0.01	0.05
Al	0.001	0.005	Sr	0.001	0.005
Si	0.01	0.05	Ru	0.02	0.1
P	0.05	0.25	Rh	0.03	0.15
K	0.01	0.05	Pd	0.006	0.03
Ca	0.0001	0.0005	Cd	0.005	0.025
Ti	0.002	0.01	Te	0.05	0.25
V	0.005	0.025	Ba	0.001	0.005
Cr	0.001	0.005	Pt	0.017	0.085
Mn	0.001	0.005	Hg	0.05	0.25
Fe	0.002	0.01	Pb	0.015	0.075
Co	0.002	0.01	Bi	0.05	0.25
Ni	0.001	0.005	U	0.1	0.5

techniques described in more detail by DeKalb and Fassel.[93] It should be noted here that line identification can be a difficult task, because the optical spectra of many lanthanide elements are very complex. A discussion of misidentifications of spectral lines of REE is also given by the authors.

2. *Inductive Coupled Plasma Atomic Emission Spectrography*

The physical properties of a plasma offer performance and operational advantages over arc and spark emission sources. The inductively coupled argon plasma is a special type of plasma that derives its sustaining power by induction from a high-frequency magnetic field. There is no electrode contact in the inductive coupled plasma (ICP) source. Thus, excitation and emission zones are resolved spatially, producing a relatively clean background spectrum which consists of argon lines and some weak band emission from OH, NO, NH, and CH molecules. This low background combined with a high signal-to-noise ratio of analyte emission produces low detection limits. The most recent development of a three-electrode direct current argon plasma, where the plasma jet is formed between two spectrographic carbon anodes and a tungsten cathode in an inverted Y-configuration results in improved stability and better detection limits than previously reported for DC plasmas. Table 7 presents detection limits for this type of plasma, defined as two times standard deviation of blank measurements. Also given is the minimum concentration to estimate quantitatively with a standard deviation of ±10%. It should be noted that these detection limits hold for pure aqueous solutions only. For most geologic problems the situation is such that it is not always possible to concentrate a sample to the desired minimum volume. Table 8, therefore, shows detection limits and minimum concentrations of REE's compared with the content of the lanthanides in 100 mg meteoritic sample, dissolved in 10 mℓ solvent.

From these tables it is clearly seen that detection limits of the ICP method are comparable to those of neutron activation and mass spectrometry. In cases where

Table 8
DETECTION LIMITS, MINIMUM CONCENTRATION TO BE ESTIMATED QUANTITATIVELY AND CONTENT OF STANDARD CHONDRITE FOR REE IN ng/mℓ[a]

Element	Detection limit	Quantitative	Chondrite
La	0.1	0.5	3.0
Ce	0.4	2.0	8.4
Pr	2.0	10.0	1.2
Nd	0.3	1.5	5.8
Sm	0.1	0.5	2.1
Eu	0.01	0.05	0.74
Gd	0.4	2.0	3.2
Tb	0.1	0.5	0.49
Dy	1.0	5.0	3.1
Ho	0.6	3.0	0.73
Er	0.2	1.0	2.1
Tm	0.03	0.15	0.33
Yb	0.02	0.1	1.7
Lu	2.0	10.0	0.31

[a] 100 mg chondrite dissolved in 10 mℓ solvent.

neutron activation fails, it is the most sensitive analytical method known until present, if one also takes into consideration that a major problem concerns preparation of solution ready for direct input in the atomizer.

Until now, few contributions dealt with investigations on the limits of the method with respect to the ultra trace region, but it is argued that similar restrictions are valid as previously discussed in the section on activation analysis. As can be seen from Table 8, the limits of a quantitative determination using the ICP method cluster around the chondritic levels for the REE. Thus it should not be a simple task to determine these elements by simple dissolution of materials with low REE concentrations, even if it is possible to raise the concentration of the sample in the solution. At least for ultrabasic rocks, a preconcentration step would be essential.

In the case of silicic samples one is in the favorable position of being able to evaporate SiO_2 completely from the matrix; therefore, somewhat larger sample amounts would lead to higher concentration of the traces under investigation. A certain impression of the limits of the method offers a test on the possibilities of the determination of Pd in iron meteorites, a problem soluble with great difficulties by neutron activation analysis. Figure 3 shows the spectrum of a blank, adjusted to iron meteoritic composition, 1 g dissolved in acid and diluted to 10 mℓ, operated with a Spectra Span III in the region 3404 to 3405 Å, on the left hand side, whereas on the right hand side of the figure the same sample spiked with a solution containing 2 μg Pd is operated within the spectral region mentioned. The most favorable peak of Pd for quantitative determination appears at 3404.58 A; it is situated on the right hand shoulder of a dominant Fe-peak in a region with appreciable background contribution. From Table 6 the quantitative detection limit (±10% rel.SD) for Pd is evaluated to be 0.03 μg/mℓ, whereas from this run a 2δ detection limit of 0.1 μg/mℓ can be deduced. This means that the quantitative detection limit for Pd should be in order of 0.5 μg/mℓ. Since Pd contents of iron meteorites vary from 2 to 9 ppm, the ICP method in this particular case works at the detection limit.

Nevertheless, ICP emission spectroscopy has been characterized frequently as a

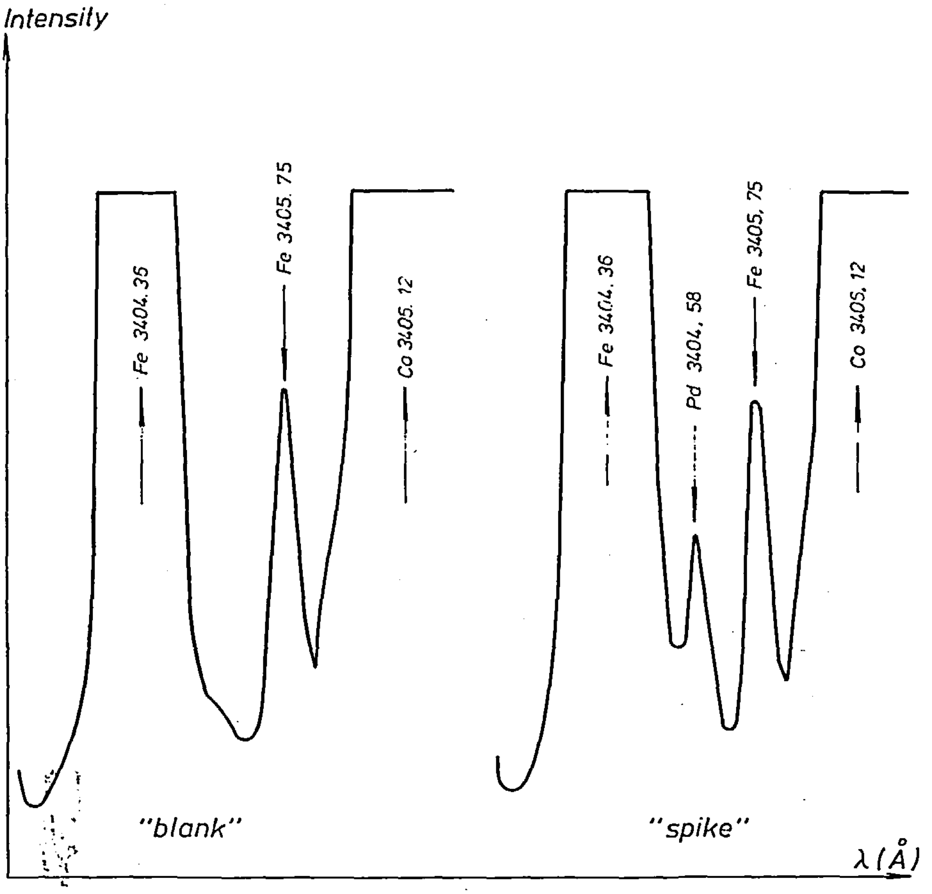

FIGURE 3. ICP—Spectrum (Spectra Span III) of synthetic iron meteorite ("blank") and Pd spiked ("spike"). Spectral window ±0.4 Å, steps of 0.025 Å.

panacea for all elemental determinations at all concentration levels. Indeed, the method fulfills many of the requirements of an ideal system for a simultaneous determination of the elements, as Fassel[94] pointed out in his award acceptance address at the ACS/CSJ Chemical Congress which was held in 1979. Besides spectral line interferences, a general problem with all methods which use a signal coming out from the atom itself, the main problems arise due to unsatisfactory fusion steps performed with the sample as well as aerosol generation processes. It should be clear from the following selected considerations on these topics that it is impossible to give instructions concerning a unique and generally applicable fusion step. Fusion is the most crucial step in the analysis by means of ICP spectroscopy, if the power of the method should be utilized to full advantage.

Simple decomposition of silicates by acids is not always practical and analysis is almost incomplete because certain minerals are not attacked at all. On the other hand, total salt concentrations obtained would be less than with alkali and metaborate fusion steps. The investigations of Uchida et al.[95] are a good example of which way a decomposition procedure should be tested. The authors treated 50 mg of powdered rock sample with 1 mℓ HCl and 0.5 mℓ HF in a Teflon vessel. After sealing the vessel and leaving it to stand for more than 4 hr at room temperature, the contents were transferred to a polypropylene bottle with 6 mℓ 4% boric acid solution. This solution was finally diluted with water to

100 mℓ and weighed. In a figure showing the effect of time on sample dissolution by the acid mixture mentioned previously, the authors reported 100% of Al and K to be leached after a standing time of 0.5 hr, whereas the leached fraction for Si and Na is given to be ~93%; Fe, Ca, Mg to be ~88%; Ti and Mn ~80%. Since the authors did their investigations on a basaltic sample, it is evident from the mineralogy that a mineral such as zircon is almost insoluble concerning this procedure. Therefore, this procedure is applicable to geologic materials with exceptional mineralogy only. By this method the following minerals have to be absent: beryll, disthen, chalkopyrite, pyrrhotin, pyrite, staurolithe, topaz, and certainly some others not examined under similar decomposition conditions until now. This effect has been observed by Uchida et al.[96] when testing the method with respect to trace elements. The authors reported on the effects of heating the decomposition mixture and the sample up to 130°C. The content of leached fractions increased with an increase in temperature. Nevertheless, the recoveries did not reach 100% for Zr and Cr.

As pointed out by Boumans,[97] the dissolution of a solid sample may not only be a time consuming and difficult procedure, but there are also risks of contamination and losses of volatile elements if the large linear dynamic range of three to five orders of magnitude is used for the determination of major, minor, and trace elements as well. For this purpose, Walsh[98] presented two methods of solution preparation for silicates which are outlined briefly. A method is described using lithium metaborate, although incomplete attack with some refractory minerals and failure to produce a stable solution of the silica when the fused mixture is dissolved in HNO_3 is evident. Nevertheless, the method seems to be applicable for a large number of silicate rocks. The rock powder (0.5 g) is fused with 2.0 g of $LiBO_2$ in a platinum crucible for 30 min on a Meker burner. The crucible is allowed to cool and placed in a 250-mℓ polyethylene beaker containing 200 mℓ of a cold 5% v/v nitric acid solution. Dissolution of the bead takes 1 to 2 hr; the solution is finally diluted to 250 mℓ. These solutions are stable over a period of several months and may be used for the determination of the major elements, plus some of the more sensitive trace elements.

The second method has been widely used for the analysis of silicate samples; it enables a more concentrated solution of the rock to be prepared because silicon is removed by evaporation. Powdered rock (0.5 g) is treated with 4 mℓ of concentrated $HClO_4$ and 15 mℓ HF. The solution is evaporated almost to dryness, cooled, and 4 mℓ of $HClO_4$ as well as 15 mℓ H_2O are added subsequently. This solution is gently warmed until all salts are dissolved, cooled, and diluted to 50 mℓ. All major elements, except SiO_2 and a number of trace elements, may be measured. It is noted by the author that this procedure may fail to attack some refractory minerals and the solution, therefore, should be carefully inspected for any residue.

Besides these limitations, it is really disappointing that under the last mentioned conditions the detection limits of the elements to be determined (Ba, Co, Cr, Cu, Li, Ni, Sr, V, Y, Zn, and Zr) are in the order of 2 to 10 ppm.

Thus it is not surprising that analysts come to a more realistic view of the feasibilities of the method. Although it has been thought the method would be generally applicable without complications at least to liquid samples (such as geologic waters, in a contribution by McLeod et al.[99]) some trace elements (Cd, Cu, Fe, Mo, Ni, V, and Zn) in sea water were determined after preconcentration of these elements. Although the ICP technique lacks the sensitivity of graphite furnace atomic absorption spectrometry, when provided relatively high preconcentration factors, the sensitivity limitation can be circumvented, and the analytical advantages of the ICP technique can be realized. The reported procedure involved a double extraction of acidified (pH about 2) sea water (500 g) using chloroform and combined ammonium tetramethylenedithiocarbamate-diethylammonium diethyldithiocarbamate followed by back extraction of the metal carbamates into nitric acid.

Since the technique of ICP spectrometry is relatively new in the analytical field, few applications to extraterrestrial material have been published. Recently, a rapid, simultaneous 17 elements analysis of Yamato meteorites was carried out by Hirano et al.[100] It was pointed out by these authors that interelemental effects have to be reduced for a better determination of samples with complex matrices, although ICP spectroscopy has very small interelemental effects. With respect to geochemical materials, these effects include emission line or molecular band interference to the objective emission line, background intensity increase mainly due to stray light, enhancement or decrease of the objective line intensity with the presence of other elements, etc.

It seems essential to draw attention to some other problems connected with sample preparation with which one is confronted generally when using ICP technique. One is the deterioration in detection performance for solutions of high acid content and which has already been discussed for nitric acid by Berman et al.[101] The other concerns metaborate-fused samples which may cause a continuous drift in the readings and usually affect the nebulizer which clogs; therefore the system becomes inoperable within some minutes after it is turned on. As described by Burman et al.,[102] a deposit on the tip of the clogged nebulizer is the culprit. This deposit, however, changes the gas flows remarkably and, thus, the sample flow. Naturally this effect may be avoided by additional dilution of the solutions, but this is objectionable since it decreases the sensitivity of the procedure.

Finally, it should be mentioned that further literature on ICP-AES techniques with respect to analysis of geological materials has been reviewed by Dinnin,[103] Boyko et al.,[104] Moore,[105] and Boyko et al.[83]

3. *Flame Spectrophotometric Analysis*

This method, in principle, is a simplified application of emission spectroscopy. In general, the number of elements whose atoms can be excited by the thermal energy of a flame is limited and dependent chiefly on the temperature of the flame employed.

As in the case for emission spectroscopy in general, experimental conditions must be very carefully standardized if reproducible results are to be obtained by the method. One factor, usually disregarded by many analysts, is the presence of substances other than those to be determined, which may cause considerable errors. Therefore, most rock analysis laboratories determine sodium and potassium and, in a few cases, lithium by flame spectrophotometric analysis employing a relatively low temperature flame, so as to excite only a few elements and hence eliminate much interference at the source. For the earth scientist, the accurate determination of the alkalis is a matter of primary importance, and an error here has considerable effect on the calculation of the norm.

In the past decades, flame emission determinations over wide concentration ranges have been carried out on terrestrial samples. Because of the limited quantities of material which are at the analyst's disposal, this method was scarcely applied to extraterrestrial matter. Since the method is primarily used for the determination of the alkalis in geologic samples, it does not seem necessary to discuss in more detail the problems mentioned earlier. In a paper by Parczewski and Kościelniak,[106] however, the interferences in the determination of K, Na, and Sr by flame emission spectrometry due to different sample components has been studied. The publication deals predominantly with the formulation of mathematical models approximating the relationship between the measured emission signal and the concentration of the sample components.

The only contribution which is worthy of note is by Köster[107] in which a simple separation technique is described for separating two- and multivalent metal cations after an acid fusion of the geologic sample. The separation step is easy to carry out, all alkalis can be determined, and the analysis is of better reliability if all constituents interfering in flame photometric determination are removed.

Although the fusion step is not of essential importance for the anion exchange separation step, three decomposition modes are preferentially applied. In the HF-$HClO_4$ decomposition step, 500 mg of the rock powder is dissolved in a mixture of 2 mℓ concentrated $HClO_4$ and 10 to 15 mℓ concentrated HF after adding 3 mℓ of H_2O to the powder. The mixture is left for 1 hr and thereafter fumed to dryness. This procedure is done twice; subsequently, the residue is fumed twice with a mixture of 2 mℓ concentrated HCl and 5 mℓ water and finally dissolved in 5 mℓ 1 N HCl. This procedure is applicable for materials containing no organic substances. If carbonates are constituents of the sample, these have to be decomposed by HCl prior to the fusion.

In the HF-H_2SO_4 decomposition step, the sample is likewise treated by a mixture of 2 mℓ concentrated H_2SO_4 and 10 to 15 mℓ concentrated HF after addition of 3 mℓ water. Care should be directed to samples containing appreciable amounts of K_2O and quartz, like granites, because of the formation of K_2SiF_6, which is sparingly decomposed by sulfuric acid. Some gneisses, however, are not attacked under the conditions described, and the decomposition step is therefore carried out using an autoclave at elevated temperatures.

The separation of the matrix elements is achieved by passing the solution obtained after the decomposition of the samples through an anion exchange resin column. Before, the resin is converted to the citrate form by treating with a 0.05 m triammoniumcitrate solution. The multivalent cations are adsorbed and the alkalis appear as citrates in the effluent.

For flame photometric purposes, the solution containing the alkalis has to be diluted for the determination of Na and K. The solution usually has to be concentrated for the determination of Li and Rb. Only in very specialized cases is the flame photometric determination of Cs possible without preconcentration of the element.

As even noted by Horlick,[108] little direct work in flame emission spectroscopy is currently being published. This is obviously due to the fact that more modern and less problematic methods are available nowadays, so FES is mainly used for the determination of Na and K in geologic samples. In this respect the method can therefore be regarded as a traditional, well-approved analytical technique. Even the fusion steps are not associated with any significant problems since most of the common alkali-containing silicates are easy to decompose under the conditions mentioned.

4. Atomic Absorption Spectrophotometric Analysis

Atomic absorption entails the determination of the absorption at the line center by using a narrow-line source emitting the given resonance line of the element. As external light sources, both hollow cathode lamps and electrodeless discharge tubes are used. The fact that light sources are required for each element is sometimes seen as a disadvantage of atomic absorption spectrophotometry (AAS), especially in such cases where multielement analysis should be carried out on geologic materials available in small quantities. Although multielement lamps are in use for certain combinations of elements, AAS analysis again is not frequently applied to extraterrestrial samples.

When using an atomizer, the flame gases are treated as a medium containing free, unexcited atoms capable of absorbing radiation from the external sources. This technique requires dissolution of the sample. Within the last few years significant developments in atomic absorption have been concerned with improvements in atomization techniques. The development of electrothermal atomizers as substitutes for the conventional flame-based systems, however, was not able to resolve the problems with geologic materials apart from very special cases. This technique, however, would enable the analyst to analyze directly solid samples to eliminate the costly and time-consuming steps necessary to put many matrices into solution form.

Since reviews in the field of AAS are really numerous, I will focus discussion on new developments in the analysis of geologic samples and select those elements to which AAS should be sensibly applied either on reason of sensitivity and/or as fruitful complements to other analytical methods. As an example, it is imaginable to extend the widely applied nuclear techniques by means of AAS to elements such as Be, Cd, Tl, and Pb, not easily estimated by the former.

Before starting this selection, attention should be paid to excellent review articles covering the field of AAS in general and its application to geologic materials in particular. These are by Horlick[108,109] as well as Moore;[105] in these the reader can find numerous references to geologic application.

The main problems of the method again should be discussed with respect to the REE, where much work has been done to apply AAS successfully. As shown by Mazzucotelli and Frache,[110] interference studies with synthetic solutions are in most cases not directly negotiable to any matrix. The excellent and detailed study of the authors shows the effects of the silicate matrix elements concerning AAS with electrothermal atomization for determining trace amounts of REE in rocks.

The interferences were evaluated by the addition of solutions of pure element salts to a europium solution of constant concentration. The interfering element to europium ratio varied from 1:1 up to 100,000:1. It has been clearly demonstrated that nearly all elements tested show enhancing effects on the atomic absorption of Eu, with Mg the only exception. The enhancing effect of alkali metals may be postulated as being caused by some chemical or physical interference and may even be attributable partially to ionization of metal atoms as shown by the absence of absorbance values, when solutions containing only Na or K were atomized at the europium wavelength. The enhancing effect of the alkalis, however, disappears if the sample solution is ashed at 1800°C, when these elements are volatilized. Concerning Fe, Ca, and Al, these elements have a relatively high absorbance at 459.5 nm, the wavelength used for the Eu determination. The interference effects are due to molecular absorption bands of oxygen compounds. The study also shows interferences caused by minor and trace elements, where both depressing and enhancing effects are observed.

The conclusion from this outstanding contribution, therefore, is the impracticality of a direct determination of the REE in the initial solution of the rock sample, even with the standard-addition method. Apart from these restrictions, it should be noted that the content of a trace element in a complex matrix is sometimes too low to reach the theoretical limit of sensitivity of the absorption. With high salt concentration, the background noise is considerable. Thus, for most of the trace elements, the detection limit is considerably higher than the sensitivity.

From these studies it becomes clear that trace elements should be free from the bulk of matrix elements. Sen Gupta[111] recently proposed the separation of the REE as a group from the matrix, but serious problems arise even when applying his method. In the first step, silicon is volatilized by HF and, as noted earlier, care should be directed to minerals not attacked by this dissolution method. Furthermore, the REE are co-precipitated with calcium as the oxalates and then separated from calcium by co-precipitation with a small amount of added iron. A concentrate prepared in this way contains the REE together with Sc, Y, Th, and the added Fe. Interelement interference studies are therefore restricted to these elements. The presence of Fe up to a 200 ppm level had no effect on the absorbance of any of the lanthanide elements in graphite furnace atomization technique. However, for Ce and La, strong negative absorption signals were noticed. The author argued that these were probably due to emission interference from the graphite furnace at the adsorption wavelengths of Ce and La. Obviously both elements have to be determined by other methods.

Furthermore, it should be mentioned that additional complications arise from interference of anions frequently used in dissolution steps. These involve halides which react with analyte atoms, allowing them to escape in molecular form, and thereby reducing sample absorbances. Methods to reduce or eliminate interference effects are numerous; a detailed survey on this subject is given by Koirtyohann et al.[112] where special attention is given to perchloric acid interferences in furnace AAS. Perchloric acid is, of course, often used in sample preparation for geologic materials. The authors showed that signal suppressions for some elements are considerable even though the charring temperatures used were well above the boiling point of the acid. Of the elements tested, Al and Tl show a significant suppression up to 95%. Even for Ag, Be, Bi, Cd, Fe, Ga, Mn, Pb, Sn, and Zn, reduction in peak absorbance is reported. No suppression (<10%) was seen for Co, Cr, Cu, Mo, Ni, Pt, and V. Perchloric acid prevents atomization of several elements even though vaporization takes place at the expected stage of the furnace cycle. It seems plausible that the acid or its decomposition products reacts with, or are sorbed on, the graphite in a thermally stable form. Decomposition or release of these residual products results in a gas phase reaction that inhibits atomization during the highest temperature phase of furnace operation. The effect, however, in most cases can be minimized by addition of ammonium carbonate or ammonium sulfate in slight molar excess over $HClO_4$. The use of the former causes fewer blank problems, but also precipitation of hydroxides, and can therefore not be added to samples outside the furnace.

AAS is, in my opinion, a suitable method for routine analysis of major and minor constituents in terms of lower capital cost and greater speed of analysis when concerning geologic samples. At present it is not possible to use solid samples for AAS except in very special cases. As shown in an excellent review on direct AAS analysis of solids by Langmyhr,[113] sample weights range from less than 1 mg up to about 20 mg, disregarding for the moment those atomization cells that allow amounts of sample up to several hundred milligrams to be atomized. Disadvantages, however, are numerous. The method is destructive, and normally only one element can be determined at a time. Furthermore, the use of small samples may introduce sampling errors and interferences may give systematic errors during the measurement of absorption.

The most serious problems arise from the fact that the influence of particle size on the atomization efficiency is considerable. If the technique of atomization of rock powders suspended in liquid-dispersing agents is applied, complete vaporization of the particles in a flame is achieved only when the particle size is reduced to below 1 μm. As it is well known to analysts, the reduction of the particle size of many types of geologic samples to below 1 μm is virtually impossible.

If atomization cells are used, a knowledge of the reactions that occur is highly desirable in order to choose the most favorable conditions and to control and minimize the effects of interferences. It should be noted that, for example, during the drying stage at 370°K some highly volatile elements and metal containing compounds (Hg) may be lost. Even in the following ashing stage the volatility of the analyte or its compounds sets the upper limit of the ashing temperature. Finally, interferences from the matrix elements remain in any case. As is apparent from the above discussion, AAS analysis on geologic samples is more or less restricted to the determination of major and minor constituents.

Recently Labrecque and Schorin[114] analyzed major constituents in laterites and compared AAS data with those obtained by X-ray fluorescence and classical methods. According to the authors, the dissolution process is the most sensitive and time-consuming step of the whole analysis. Besides this disadvantage, AAS has the difficulty of determining major sample constituents without a large degree of dilution. Interferences for silicates, especially the interelement effects of Al, Si, and/or Fe were first thought to be eliminated by the use of the dinitrogen-acetylene flame. This, in fact, was not the case. The authors described a much more efficient system to eliminate the interelement effects, namely the fluoboric-boric acid system. This system has been successful for Fe, Al, and Si, but not for Ti. The extremely low values for Ti obtained by AAS are obviously an effect due to incomplete decomposition of the material and apparently caused by the presence of different titanium minerals. For example, ilmenite ($FeTiO_3$) is much more soluble in acids than rutile (TiO_2). On the other hand, the authors themselves did not observe visible particles in the solution. Obviously an optical inspection of the solution is not sufficient in such cases where suspended minute minerals, almost unattacked by the fusion step, are to be expected.

As noted earlier, the method is a powerful tool in the determination of trace elements in certain geologic materials, such as coal and other carbonaceous matter. The solid sampling technique of AAS is suitable for trace analysis and it is well described in the literature. I would recommend the paper by Langmyhr et al.[115] on the determination of Cu, Ni, and V in coal and petroleum coke. Preliminary measurements were made to establish the optimum drying, ashing, and atomization temperatures and times. It was found necessary to base the analysis on measuring peak areas. Care also has been directed to the choice of the standards. It was established that determination against a solid reference material, an aqueous primary standard, or by the method of standard additions, is feasible.

As mentioned earlier, AAS of trace elements in geologic samples requires more or less complicated separation or preconcentration steps which usually are, at the very least, very time-consuming. In scientific research work I would recommend these procedures, which are in most cases susceptible to contamination, for the analysis of elements not easily determined by other methods. From the spectrum of elements falling in this category (Be, B, In, Sn, Tl, Pb, and Bi), I selected a paper by Vilcsek and Lohmann[116] concerning the determination of Be in meteorites, one of the few publications in which the method of flameless AAS is applied to extraterrestrial matter. But this was not the only reason for selection. The paper drastically demonstrates what may happen if little attention is paid to the decomposition step of the sample. In some cases of determining Be it was found that under the conditions and temperatures used to decompose silicates with a mixture of $HF\text{-}HClO_4$ a part of the Be is obviously volatilized and thus not determined. The volatile Be compounds therefore were first expelled by heating the samples in a quartz tube at 400°C in a nitrogen atmosphere and condensed in a liquid nitrogen-cooled tube. From this condensate the beryllium acetylacetonate could be extracted and the element could be determined by flameless AAS. After this procedure the sample was dissolved with a mixture of $HF\text{-}HClO_4$, the beryllium again extracted and determined. The results show that up to 60% of the Be may appear in the form of a volatile compound, volatilized during the dissolution step. Due to the small contents of beryllium in the meteorites investigated (25 ppb up to 313 ppb), it was not possible to identify this compound. Alternatively, it may be the case that this compound is not formed until the decomposition procedure due to different forms of chemical binding of the element in the various mineral phases of the sample.

Finally, a procedure developed for the determination of Tl in minerals and coals by AAS should be mentioned. Berndt et al,[117] described a very efficient preconcentration method for this element after dissolution of the sample, complexing Tl with dithiophosphorus acid-0,0-diethylester, ammonium salt, and adsorption of the complex onto an activated carbon filter. By treating the activated carbon with nitric acid, a trace concentrate is obtained practically free of matrix elements from which the Tl can be determined without interferences by various spectroscopical methods. As shown by the authors, AAS detection limit using graphite furnace technique is as low as 0.01 μg/g; when applying ICP-AES a detection limit of 2 μg/g is reported. This example shows that in certain instances AAS could be the method of choice with respect to detection limit as well as precision and accuracy.

5. Molecule Absorptions Spectrophotometric Analysis

This method of analysis is based on the conversion of an element to a more or less strongly colored compound in solution, or sometimes in colloidal suspension, and is in principle applicable in one form or another to a very wide range of elements. The colored solution differentially absorbs light of different wavelengths, the amount of this absorption being related to the concentration of the colored substance. Naturally colorimetric methods are also included in the chapter.

The ease and simplicity of spectrophotometric methods often continues to be a compelling reason for their selection for analysis of geologic material, although many new highly sensitive analytical methods are at the scientist's disposal. This continual increase in the number of applications is documented by excellent and extensive review articles by Hargis and Howell.[118-119]

In modern geochemical research, however, where the interest is largely centered on those elements present in lower concentration ranges, it is often impracticable to apply spectrophotometric analysis to elements of the periodic table, which may be present as traces in the chemical reagents used. The more complicated or even sophisticated the working procedure looks like, the more reagent blanks may impose their own lower limit on a determination.

Today two standard textbooks for colorimetric and spectrophotometric determinations of various elements should be mentioned. The first, who presented reliable and accurate methods for very many trace elements in geologic material, was Sandell,[158] more recently, spectrophotometric methods were selected and discussed by Koch and Koch-Dedic.[14]

In the ideal case, isolation of the component prior to its determination is not required because the color-forming reaction is so specific that interferences due to the presence of other elements is negligible. Spectrophotometric analysis thus is very rapid and, indeed, provides the principle for the determination of elements like Si, Al, Fe, Mn, Ti, and P in rock analysis. In 1956 Shapiro and Brannock[120] published a rapid, simple, and direct method, though not of the highest possible accuracy, for the colorimetric determination of major and minor constituents in rock samples as well as samples of rock-forming minerals. The analytical scheme is outlined by Vincent[121] and has been modified individually by those laboratories which still apply this — for many purposes sufficient — analytical procedure at present. At the very beginning of analytical investigation on lunar samples, Wiik and Ojanpera[41] applied colorimetric methods to estimate the contents of Si, Ti, Mn, and P.

Care should be required when certain trace elements (as, e.g., Si, P, Fe, Zn, Cd, Au, Hg, Tl, and Pb) are to be determined by spectrophotometric means and when chemical isolation of the particular constituent is needed prior to its determination. Contamination not only from the reagents used should be considered, but also contamination due to manipulation in laboratories not suitably equipped.

For a more detailed discussion of modern spectrophotometric methods I have selected the platinum metals. It is very well known that this kind of data for terrestrial materials is either extremely limited or nonexistent. Basic and ultrabasic rocks have been more extensively studied, but the bulk of the data are for Pd and Pt only. A similar situation is given for extraterrestrial matter, where data is mainly concentrated for Ru, Pd, Os, Ir, and Pt. Data again is sparse, but one has tried anyway to cover the whole group of these elements.

This fact, however, is in striking contrast to the immense number of spectrophotometric reagents recommended for the determination of the platinum metals, as listed by Beamish.[122] Since this publication was written the number of reagents proposed has been considerably increased, without any noticeable effect on the situation in the geochemical field, although concentration ranges covered by some reagents extend well below the parts per million range. It is out of the question that spectrophotometric determination would be the logical consequence due to the fact that this group of elements brings up many problems and difficulties in any of the instrumental methods today generally applied in geosciences.

The reason for this contrast is mainly due to the fact that most of the methods developed are not directly applied or attempted on to geologic samples. This application is sometimes counterfeited in the title of a publication as, e.g., in that by Gowda et al.,[123] in which the simultaneous spectrophotometric determination of Pd (II) and Au (III) with methiomeprazine hydrochloride (analysis of alloys and minerals) is announced. Although the method is extensively and carefully examined, the authors state under the heading "Analysis of Alloys and Minerals of Gold and Palladium" that the minerals stibiopalladinite, sylvanite, and porpezite were not available for analysis. Hence, synthetic mixtures containing palladium, gold, and other metals usually contained in these minerals were prepared. Obviously this preparation has been achieved by mixing of soluble compounds in proper proportions. This clearly circumvents the difficulties of the dissolution problems of the noble metals, and the comment by Beamish[122] is still valid that despite analytical efforts for more than a century, no procedure has been recorded that can be used with confidence for the direct determination of each of the noble metals in primary deposits. The most valuable contribution in this respect is a paper by Sen Gupta,[124] who tried to overcome decomposition difficulties in the spectrophotometric measurements of platinum group metals in meteorites. Additional literature on this subject may be found as well in this contribution.

D. Mass Spectrometric Analysis

In principle, this method is based on the separation of charged particles according to their mass/charge ratio. During the past years mass spectrometry has gained increasing significance for earth scientists, especially after spark source mass spectrometry for geologic samples was pioneered by Taylor[125] in 1965, because detection sensitivity could be raised considerably. Moreover, virtually all elements of the sample are atomized and ionized with nearly equal sensitivity.

Precision of the method could be raised by the introduction of electrical ion detection as well as multielement isotope dilution on solid and dissolved samples. Early applications were restricted to those elements for which tracers were available; thus the method was first used for hydrogen- and later on for nitrogen- determinations. The development of electromagnetic separators and their use in providing many stable tracers has permitted a rapid expansion of the method to practically all elements of the periodic table.

The increasing influence of mass spectrometry on the analysis of inorganic materials, however, has not been taken into consideration until the present. In the fundamental reviews on mass spectrometry by Burlingame et al.,[126,127] no coverage of inorganic applications is given. Only a small paragraph in a review article by Dinnin[103] deals with geologic applications. One of the most valuable reviews on the application of mass spectroscopy to geochemical and cosmochemical problems is that by Hintenberger.[128] The review presents a short description of the instruments, and some few methods of application to terrestrial and extraterrestrial material are mentioned.

As practiced in the previous sections, the author will again direct special attention to carefully selected and tested sample preparation methods, generally less frequently considered in most review articles but of eminent influence on the reliability of the results. The preparation of the material for introduction of an element into the mass spectrometer, however, is a critical step in stable isotope geochemistry. This especially is the case if a gaseous compound is desired, where quantitative yields are necessary in order to prevent isotope fractionation during sample preparation as well as to prevent interferences in the mass spectrometer.

Since organic geochemistry is reviewed sufficiently by Burlingame et al.[126,127] and there is an excellent article by Hayatsu and Anders[129] on organic compounds in meteorites, special attention should be directed to inorganic sampling problems. Moreover, methods for the extraction of organic compounds are more or less standard preparation techniques; separation of the components or their derivatives are carried out mainly by gas chromatography, whereas identification is done by mass spectrometry. Thus the most serious problem is contamination. Much work has been invested in overcoming contamination, such as gas chromatography of diastereomeric derivatives showing that the Murchison meteorite contains at least 18 indigenous amino acids. Furthermore, so-called safeguards against contamination have been applied using deuterium rather than light hydrogen during procedures of synthesis.

Concerning stable isotope geochemistry, I selected oxygen, sulfur, and the system samarium-neodymium for a more detailed discussion. The isotope effects in geologic samples result as a consequence of differences in the physicochemical properties due to the mass differences of different isotopes. These mass differences are most pronounced among the light elements.

Oxygen is chosen because it is the most abundant element on earth and the moon, as well as in stony meteorites. Moreover, it occurs in terrestrial samples in gaseous, liquid, and solid compounds. These facts make the element one of the most interesting in isotope geochemistry. Literature sources are numerous, but reference is made here only to a book by Hoefs[130] where, besides oxygen, a number of selected elements are reviewed.

In almost all cases, CO_2 is the gas used in the mass spectrometric measurements. The liberation of oxygen from silicates entails most of the difficulties so far. On the other hand, information on the oxygen isotopic composition will give a deeper insight into effects of magmatic crystallization and differentiation of magmatic rocks. Moreover, the oxygen isotope ratio may serve as an indicator of temperature of formation of igneous and metamorphic rocks.

Extraction of oxygen by reaction with fluorine appears to be the most reliable procedure applicable to a wide variety of minerals. The experimental basis and its application has been published by Taylor and Epstein.[131] The authors discuss extensively the limitations of the method. Quantitative yields of oxygen are readily obtained from most rock-forming minerals by the fluorine extraction process. Problems, however, have been encountered with olivine, magnetite, epidote, and garnet. It has been shown by the authors that reaction yields are between 20 to 40% of the oxygen of the mineral, if olivine and magnetite are ground to only <100 mesh. Yields are considerably increased if these minerals are ground to <200 mesh. Maximum yields are obtained when these minerals are ground finer than 200 mesh and reacted with one and a half times the normal amount of fluorine and twice the normal amount of hydrogen fluoride, at the highest practicable temperature of 490 to 520°C for 2 to 3 days. If nonvolatile fluorides such as CaF_2, NaF, and MgF_2 are formed during reaction, these could provide an armor coating on the mineral grains, slowing down further reaction. In any case, the oxygen is subsequently converted to CO_2 for mass spectrometry because carbon dioxide lies in a region of the mass spectrum that is less contaminated with background impurities. In addition, oxygen is a more reactive gas than is CO_2, and could therefore react with an easily oxidizable substance, so isotopic fractionation might occur. Nevertheless, the converting process is sometimes avoided and oxygen gas itself supplied to the mass spectrometer, as carried out by Clayton and Mayeda[132] and Becker and Epstein.[133]

All the raw oxygen isotopic data usually have to be corrected, among other things, because of impurities of the samples analyzed and extraneous oxygen from the commercial fluorine cylinder. The latter may be circumvented by the replacement of fluorine by oxidizing agents such as BrF_5, BrF_3, XeF_2, or CoF_3.

BrF_5 has been applied by Clayton and Mayeda[134] to mineral samples ranging in weight from 5 to 30 mg. The reactions are usually run at 450°C for 12 hr with an approximately fivefold excess of reagent over stoichiometric requirements. The authors also tested BrF_3, but finally recommended the use of BrF_5 due to its higher vapor pressure. Both reagents have several advantages over fluorine; one of which is that the reagents may be readily distilled to make them completely oxygen-free.

Nevertheless, the analytical procedure is very time-consuming even if oxygen isotopic compositions of total rock samples are concerned and no mineral separations are carried out in addition. It is, however, evident that only limited interpretations can be made using total rock sample data. More significant conclusions can be made by determining the distribution of oxygen isotopes among the mineral phases of a rock.

More detailed information on the sample preparation is found in publications by Mayeda et al.[135] as well as Onuma et al.,[136] where the method is applied to mineral phases of lunar rocks. But most of the literature deals with oxygen isotopic studies of substances, where the oxygen may be liberated by simple conventional reactions.

Sulfur is selected because this element is present in nearly all geologic materials: as a minor component in igneous and metamorphic rocks, in the biosphere, in ocean water and marine sediments, and finally as major component in ore deposits. A more detailed discussion may be found in the book by Hoefs[130] and an article by Nielsen.[137]

The gas used for mass spectrometry usually is SO_2, but sulfur hexafluoride has some advantages over sulfur dioxide concerning mass spectrometric determination. SF_6 is chemically inert and not sensitive to moisture nor adsorbed on the walls of the vacuum system. Furthermore, fluorine has only one stable isotope and no correction is needed for the presence of other isotopes. Hulston and Thode[138] used SF_6 gas prepared via silver sulfide reacting with elemental fluorine for measurements of sulfur isotopes in meteorites. The method has been tested extensively by Puchelt et al.[139] where difficulties in routine work with respect to handling of the extremely reactive agent are described. The authors were able to show that elemental sulfur and many metallic sulfides react rapidly and completely with bromine trifluoride. Low yields were reported on the other hand in the case of pyrrhotite, troilite, and digenite. Finally, Rees,[140] in a remarkable contribution was able to show that the poor agreement between laboratories measuring sulfur isotope ratios was due to memory effects from the mass spectrometer, caused by slow flushing of SO_2 from the mass spectrometer inlet line. Difficulties do not arise, however, when SF_6 is used.

The samarium-neodymium (Sm/Nd) system illustrates the mass spectrometric determination of elements usually prepared as solid compounds or as solutions. The Sm-Nd system is unique in comparison to the other long time-scale geochronometers in that both the parent and daughter element are refractory in their cosmochemical behavior. The Sm/Nd fractionation during condensation of the solar nebula should therefore be small or even zero as Boynton[141] pointed out. On the other hand, the fractionation of Sm and Nd which can occur in magmatic processes is substantial; therefore, most of the variation of the Sm/Nd ratio in the earth today is probably the result of the earth's internal differentiation. As has been shown by De Paolo,[142] the Sm/Nd system adds new significance to the isotopic variations and the transport considerations of the crust-mantle relationship of the earth. The method has been described and applied to lunar samples by Lugmair and Carlson.[143,144]

The total rock samples and each of the mineral separates were initially dissolved in HF and $HClO_4$ in a Teflon® reflux unit, then redissolved in high-purity 2 *N* HCl and split into two aliquots. One split was spiked with a mixed tracer solution, highly enriched in Sm-149 and Nd-146, for elemental concentration determination. The REE in each aliquat were subsequently isolated as a group by a 2 *N*/4 N HCl ion-exchange column in H^+ form (100 to 200 mesh), followed by the separation of Sm and Nd on a micro ion-exchange column in NH_4^+ form (200 to 400 mesh) using 0.2-*M* α-hydroxyisobutyric acid adjusted to pH 4.495 as an eluent. Precise isotopic ratios for each sample were measured mass spectrometrically.

Sm and Nd isotopic ratios recently have been measured in some chondrites and the Juvinas achondrite by Jacobson and Wasserburg.[145] From these data the authors have selected a new set of self-consistent, present-day reference values for the "chondritic uniform reservoir" (CHUR). This caused a small but significant change in the CHUR evolution curve. Some terrestrial samples of Archean age show clear deviations from the new CHUR curve. It has been shown that a variety of discrepancies with most earlier meteorite data exists which includes determination of all Nd isotopes and Sm/Nd ratios. A possible source of error might be less precise analytical methods. As has been discussed earlier, the problem eventually can be restricted to the sample dissolution process. Although the mineralogy of lunar and meteoritic samples is not complicated as opposed to terrestrial samples, it may be the case that some minor portions of the material are not at all attacked by the HF-$HClO_4$ mixture. Contamination is of course less probable when dealing with REE.

Spark source mass spectrometry (SSMS) at last was introduced by Taylor[146] in 1965 to the multielement analysis of geologic samples. Since that time the method has been used in geo- and cosmochemistry to examine terrestrial and lunar samples, meteorites, tektites, and minerals. As Taylor already noted, the problems associated with sample preparation are intensified because of the small amount of sample consumed. Homogeneity and contamination are still the main problems if the method is extended to the determination of traces constituents in the parts per million and sub-parts per million range, respectively.

In the fields of geochemistry and cosmochemistry the completeness of analysis is particularly important, a requirement fulfilled by SSMS to a high degree. All elements from Li to U have been analyzed by this means. The detection limit for many elements ranges between 1 ppb and 100 ppb; in certain cases, concentrations less than 1 ppb could be detected. As already discussed in previous sections, detection limits can deteriorate considerably due to interferences of spectral lines, depending on the composition of the sample. Recently Beske et al.[147] reviewed SSMS as an analytical method extensively. Valuable instructions are given with respect to precision and accuracy of the method. In this review attention is drawn especially to the homogeneity of the samples, the preparation of the sample, the type of analysis selected and the detection system. Standard deviations between 10 to 40% are normal if internal standards and photoplate detection systems are used. Significantly better results are obtained by more elaborate sample preparation and the application of electrical ion detection. Accuracy depends on the type of analysis selected and the thoroughness with which it is carried out. Results are considerably influenced by the calibration procedure and the application of isotope dilution analysis (SID-SSMS).

With respect to the method using a standard sample, standard rocks, well analyzed meteorites, etc. are necessary. Usually the powdered rock sample is mixed with ultra-pure graphite and briquetted to rod-shaped electrodes. In order to avoid problems with regard to sample heterogeneity and the lack of suitable standard samples, chemical dissolution of the samples is recommended. The relative sensitivity factors are then determined from the analysis of standard solutions which are treated in the same manner as the sample solutions. The application of this method is demonstrated by Jochum et al.[148] for quantitative multielement analysis of geologic samples using SSMS.

It is out of the question that analytical research on lunar samples also pushed along sample preparation technique for spark source mass spectrometric means. An outstanding contribution to this field certainly is that by Morrison and Kashuba[149] in which sample and electrode preparation is elaborated for multielement analysis of standard rocks with regard to the analysis of moon samples. The authors used In_2O_3 as internal standard and blended the sample-standard mixture with graphite or silver powder as conductors. In_2O_3 has been selected as an internal standard since the availability of the pure oxide allowed its use in a chemical form similar to the unknown elements. Moreover its concentration in undoped standard reference rocks was below the detection limit of the method. Small-sized samples on the other hand preclude the precise addition of an internal standard; therefore, independent determination of an existing matrix element is recommended. It should be noted that the application of silver as conductor prevented the calculation of Ni and Cu due to the relatively high concentrations of these elements in the silver.

Luck et al.[150] used SSMS for the determination of concentrations of some geochemical relevant elements in drill cores of a uranium deposit by mixing the samples with silver powder. Since Ni and Cu are included in the number of geochemical relevant elements, it is surprising that no comment is given with respect to a possible contamination. Especially in the case for Ni, where throughout the depth-profile of the deposit the content varies between 10 to 20 ppm; this eventually may be the order of Ni-contamination from the conductor material.

As noted by Vandelannoote et al.[151] SSMS is a rather time-consuming method, but allows the detection of about 20 elements of geochemical interest down to the parts per billion level. The only advantages contrary to neutron activation analysis is the quite uniform elemental sensitivity and the possibility of determining elements such as Sn and Pb not suitable to the radiochemical technique. Since the relative sensitivity factors appeared to be independent of the salt content of the graphite electrodes, a physical preconcentration is proposed by the authors. After filtration of the water, the sample was acidified to pH 1 with ultrapure HNO_3. Milliliters (250) were subsequently evaporated on 300 mg spec-pure graphite. The powder was pressed into electrodes and sparked. It is out of the question that analytical research will yield a wealth of information on the trace element behavior in geothermal waters, although precision of SSMS is, by a factor of about two, worse than that obtained from activation analysis.

Isotope dilution has the advantage of a standard-free method yielding absolute concentrations directly, and therefore is the most accurate technique for determining trace elements in geochemical materials. The utilization of isotopic internal standards virtually eliminates such analytical problems as quantitative recovery and instrument calibration.

Systematic errors may be due to contamination from reagents, apparatus or the laboratory atmosphere, interferences between elements with isobars, calibration of the tracers, etc. The most prominent errors are certainly chemical ones, such as incomplete decomposition of the sample, incomplete mixing with the tracer, and isotopic fractionation during chemical treatment if the recovery is not quantitative. The latter effect is most probable for very light elements only. More serious are errors caused by incomplete conversion of the element, normal and tracer into one chemical form. These problems are discussed in more detail by Webster,[152] a contribution still valid in modern SID-MS.

Due to the outstanding significance of the REE in geochemistry and cosmochemistry special attention should be paid to this group of elements. Nevertheless, sampling and dissolution problems may be generalized, if the sample exhibits a more complex silicate matrix. In a standard contribution to SID-MS by Schuhmann and Philpotts[153] an acid decomposition is recommended by adding a mixture of $NClO_4$ and HF to the sample plus spike. As mentioned earlier, this acid mixture fails if certain REE-containing minerals are present which are not or eventually partially decomposed even at elevated temperatures. It is really of interest that very little reference is made in the literature to the use of perchloric acid-hydrofluoric acid mixtures for the decomposition of silicates. Fortunately the mineralogy of extraterrestrial materials is such that no substantial problems arise.

These difficulties are sometimes felt and circumvented by the application of multielement isotope dilution technique to undissolved samples. In these cases, described by Jochum et al.[148] the spike solutions are added to the graphite, dried in a Teflon beaker, and finally mixed with the samples for 1 hr in an agate mill. It is evident that a persistent difficulty of this technique is the uniform mixing of the sample with the spiked graphite.

This method is also used by Nance and Taylor[154] and Taylor[155] for geochemical investigations on sedimentary rocks and lunar samples, respectively. The enormous advantage of the homogeneity of the sample after its decomposition is sometimes approximated by modifications, such as new electrode dies and the use of ion beam choppers extends the exposure time for abundant isotopes. This enables a larger amount of sample to be exposed to the spark and thus avoids the problems of spot sampling in heterogeneous samples.

In a paper by Knab,[156] the method of spiking the solid sample with the enriched isotopes is defended. His argument is based on the observed overlap of the mass spectra of the trace elements by the major elements of the sample. This is due to the formation of molecules, an effect which is essentially less when the sample is sparked in the undissolved state. The work done by Knab is without doubt an outstanding contribution to the distribution of trace elements in carbonaceous chondrites, which are generally considered to represent the most pristine samples of solar system material. Knab added information especially to those elements, which are to be determined with considerable difficulty by other methods as, e.g., Ge, Zr, Sn, Te, Hf, W, Re, Pt, and Pb. A more detailed description of sample preparation using this technique is given in a contribution by Knab and Hintenberger[157] in which advantages and disadvantages are discussed in more detail.

Nevertheless, dissolution and separation of elements to be determined provide advantages in the analysis of terrestrial and extraterrestrial matter as has been demonstrated throughout this article. Due to the exceptional progress in the development of instruments, it seems sometimes amazing that a so called "simple" dissolution step can be a considerable difficulty in the utilization of the full power of an "instrumental" method. It would certainly be desirable to focus more attention on these essential chemical steps, although this is of course not an attractive field of interest nowadays.

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