THE USE OF INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY IN ENVIRONMENTAL SURVEYING AND GEOCHEMICAL PROSPECTING

MAGNE ØDEGÅRD

Geological Survey of Norway, P.O.Box 3006-Lade, N-7002 Trondheim.

Abstract—This study emphasizes the relevance of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) as an analytical technique for metal ions in solutions, primarily due to the wide coverage of elements and low detection limits; qualities which are of particular significance in environmental investigations and geochemical prospecting. Such activities normally use solid geological materials as a sample medium, and major focus is directed towards the preparation of sample solutions, an important step in the total analytical procedure, and which may be of great significance for the final interpretations and conclusions. Geological materials rich in silicate minerals have traditionally been considered as resistant against mineral acids, except HF. Studies at the Geological Survey of Norway, however, have shown that many silicate minerals have considerable solubility in mineral acids, such as HCl and HNO_3. A synopsis of the results of these studies is presented. The possibility of introducing unwanted elements bound in the lattice of silicate minerals is noted, contributions which in extreme cases may disturb, or even overshadow, the effects which are to be studied. A major intention has been to demonstrate some of the many problems and pitfalls related to geochemical and environmental studies based on acid extraction of geological materials, and to stress that such activities require multiprofessional knowledge at all stages from planning to the final conclusions.

Introduction

Information on the chemical composition of geological materials is of fundamental importance within many branches of geoscience and related fields. In the early days of development of mineralogy and petrology, the classical wet chemical analytical methods were the only ones available, and used mainly for the determination of major elements for the characterisation and description of minerals and rocks. Since then, an intensive research in analytical inorganic chemistry has led to the development of rapid and accurate instrumental analytical methods with good element coverage and detection capabilities. Among those techniques, ICP-AES is one of the most applicable, especially within geochemical prospecting and environmental investigations. For these particular activities, however, the choice of sample type and preparation will be of vital importance in reaching a meaningful conclusion.

Geochemical ore and mineral prospecting

The application of geochemical principles in the search for ore and mineral deposits has long traditions, and techniques based on such principles are today valuable both as independent methods and as supplementary procedures for geophysical and geological methods.

Geochemical prospecting assumes that dispersion of elements from the deposit has taken place, and that the elements have been taken up or collected by some medium outside their source. Dispersion of elements from a source can take place either in the form of particles or as solutions, but also in some cases in the form of gases, and the dispersion is effected through transport by ice, water or air. A variety of media have been studied and used in geochemical prospecting, e.g. stream water, stream and lake sediments, mineral soils, morainic materials, humus and different types of vegetation. Among these, different types of sediments have been used successfully for many years.

Environmental investigations

Control and surveillance of the environment is of vital importance for all forms of life, and has become an activity with high political priority. A great deal of the damage to the environment is represented by pollution, which again is a typical result of today's complex, industrialised society. However, pollution of the environment can also, in some cases, take place in nature even without any human activity. This phenomenon is normally caused by ore or mineral deposits, or other occurrences with elevated element concentrations. No matter whether a pollution is caused by human activity or by nature itself, the consequences will be the same, and the methods for determining the degree and cause of the pollution will also be much the same.

Problems common to geochemical prospecting and environmental investigations

Both geochemical prospecting and environmental pollution studies have three basic elements in common, namely:

1. A primary source for the supply of chemical elements.
2. A mechanism for dispersion of these elements.
3. A medium for picking up or collecting the elements.

A common goal will also be to determine quantitatively and selectively the elements or element compounds which have been supplied to the medium from external sources. Most geological materials contain various amounts of most chemical elements, and it is unrealistic to find an analytical procedure where analyte elements present in the medium beforehand will escape analysis.

There are, in principle, two possible modes of analysis: (1) total analysis; (2) partial analysis based on some form of extraction. This immediately raises many important questions. In the case of total analysis, what are the absolute and relative amounts of analyte elements primarily present in the medium compared to the amounts supplied from external sources? In the case of partial analysis the same question is significant, but two additional important questions are: what amounts of analyte elements are brought into solution during the extraction, and how selective is the extraction?

Total analysis

In all methods determining the total element content it is not possible to distinguish between analyte elements primarily present in the medium and elements supplied to the geological system from external sources.

Total analysis by ICP-AES requires that the samples are brought completely into solution. This is normally done either by fusion with $LiBO_2$ followed by dissolution in dilute acid, or by dissolution in HF in combination with other mineral acids, followed by complexing of free HF with H_3BO_3. Both these techniques introduce considerable amounts of salts which generally complicates the subsequent analysis.

Partial analysis

It is evident that the use of total analysis can introduce many uncertainties in geochemical and environmental studies, and techniques based on partial extraction are normally chosen. Two factors will be especially important in relation to the extraction, namely:

1. The extraction attack should be strong enough to bring the secondarily supplied elements or element compounds to be studied into solution.
2. The acid attack should influence the primary sample minerals as little as possible in order to avoid introduction of unwanted elements.

Unwanted elements in this context are especially analyte elements primarily present in the geological material, and which at the same time are released during the extraction.

Partial extraction of geological materials

Most geological materials used as the medium in pollution studies or geochemical prospecting consist mainly of rock material rich in silicate minerals. The type and amount of silicate minerals can, however, vary within wide limits, and are largely dependent on the type of parent rock material. The rock-forming silicate minerals as a group have traditionally been considered as largely insoluble in mineral acids, except HF. This is not correct. Systematic research at the Geological Survey of Norway [1,2] has shown that a lot of silicate minerals have considerable solubility in mineral acids, such as HCl and HNO_3. Some silicate minerals even show a solubility of practically 100 %, while some are nearly insoluble. Graff & Røste [1] have shown that a general parameter for the solubility of silicate minerals seems to be the ratio between the number of metal atoms in the mineral lattice, except Si, and the number of Si atoms. Thus, with a ratio below 1, the mineral has little solubility. With a ratio above 2.4 the solubility is high. In the range between 1 and 2.4 the solubility can vary considerably. To give some examples:

The end member of the plagioclase series, anorthite ($CaAl_2Si_2O_8$), with a theoretical ratio equal to 1.5, has a very high solubility. The other end member, albite ($NaAlSi_3O_8$), with a ratio equal to 0.67, accordingly has a very low solubility (Fig. 1).

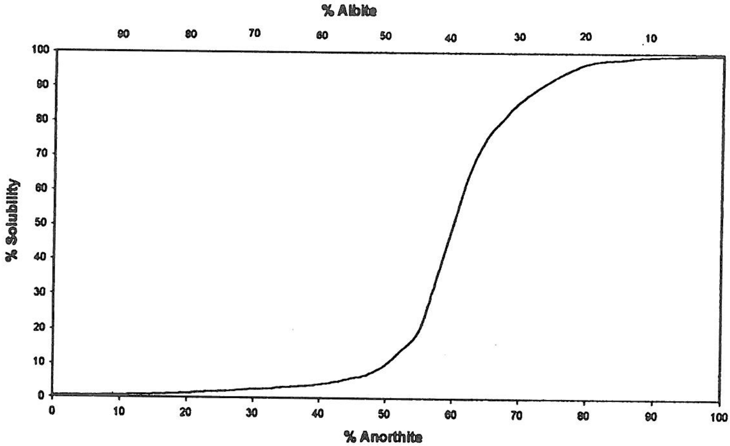

Fig. 1. Solubility of plagioclase feldspar.

Muscovite, with the common formula $2H_2O.K_2O.3Al_2O_3.6SiO_2$, and a ratio equal to 1.33 has a very low solubility, while biotite, with a composition ranging mainly between $(H,K)_2(Mg,Fe)_4(Al,Fe)_2Si_4O_{16}$ and $(H,K)_2(Mg,Fe)_2Al_2Si_3O_{12}$, and a ratio normally between 1.7 and 2.0, has a high solubility. As a digression, this explains also why biotite is a much better soil fertilizing mineral than muscovite for the supply of K_2O, even though muscovite normally has a higher K_2O content than biotite [3]. The solubility studies of silicate minerals are thus of great value within many fields, and in relation to pollution studies and geochemical prospecting the most important aspect will be the release of analyte elements bound in the lattice of the primary silicate minerals. Evaluating such contributions can now be done in many cases, provided that knowledge of the basic geochemical distribution laws and type of rock material is at hand.

Disturbing elements can also be introduced from many accessory minerals which usually occur in geological materials. Faye [2] has done a separate study of the solubility of some resistant accessory minerals, and a more comprehensive solubility study of silicate rocks covering the whole range from acidic to ultramafic rocks. These studies were primarily undertaken to ascertain the amount of major and trace elements which can be introduced during acid extraction procedures used in geochemical investigations.

Four general conclusions can be drawn from the extraction investigations, namely:

1. The extraction yield for the various elements of a rock sample varies strongly within one and the same sample.
2. The extraction yield for each single element of a rock sample varies strongly from sample to sample.
3. The extraction yields for all elements of a mineral are equal.
4. The extraction yields for the elements of a mineral in a rock sample are independent of the concentration of the mineral.

The solubility tests of silicate rocks were based on certified geological reference materials. Table 1 shows some of the obtained results.

Table 1. Range of extraction yield (extracted amount of element as percent of total content) for some selected elements based on extraction of 24 international geological reference materials with 7N HNO_3 (Faye 1982).

Element →		Fe	Ba	Sr	Cr	Ni	Zn	Cu	Pb
Extraction yield (%)	Low	1.7	2.0	1.7	0.4	8.8	7.6	~100	~100
	High	85.0	88.3	80.3	87.2	100	94.2	100	100
	Mean	46.4	27.8	38.3	38.1	50.3	56.9		

The elements are specially selected to cover actual elements in an environmental survey of offshore oil drilling [4]. In this activity, Ba is used in the form of barite ($BaSO_4$) as a weight agent, and this metal is therefore commonly used as a tracer in monitoring the distribution of drilling fluids in the marine environment. Sr is also a typical component of drilling fluids and is likewise used as a tracer for contamination control. The other elements are included because they are of particular toxicological interest.

Overview of the ICP-AES method

The ICP-AES method used for solid samples at the Geological Survey of Norway is accredited according to the European Standard EN 45001, and is based on autoclave extraction at 120°C of 1 g samples in 20 ml 7N HNO_3 in closed borosilicate bottles. An overview of the analysed elements, together with their analytical lines and lower limits of determination, is presented below. Second-order lines are marked with an asterisk. The lower limits of determination (LLD) refer to the original solid sample, and assume a sample weight of 1 g and a final analytical volume of 100 ml.

Elements and wavelengths		LLD	Elements and wavelengths		LLD
Si	288.1 nm	100 ppm	V	292.4 nm	1 ppm
Al	309.2 "	20 "	Mo	202.0 "	1 "
Fe	259.9 "	5 "	Cd *	228.8 "	1 "
Ti	334.9 "	1 "	Cr	267.7 "	1 "
Mg	383.2 "	100 "	Ba	493.4 "	1 "
Ca	317.9 "	200 "	Sr	421.5 "	2 "
Na	588.9 "	200 "	Zr	339.1 "	1 "
K	766.4 "	100 "	Ag	328.0 "	1 "
Mn	257.6 "	0.2 "	B *	249.6 "	5 "
P *	214.9 "	10 "	Be	234.8 "	0.2 "
Cu	324.7 "	1 "	Li	670.7 "	1 "
Zn	213.8 "	2 "	Sc	361.3 "	0.2 "
Pb*	220.3 "	5 "	Ce	418.6 "	10 "
Ni	231.6 "	2 "	La	379.4 "	1 "
Co	228.6 "	1 "	Y	371.0 "	0.2 "

Details on instrumentation and operating conditions are given elsewhere [5]. Calibration is based on synthetic standards, and accuracy is controlled with reference materials.

Conclusions

The extraction studies referred to in this paper [1,2] have shown that the amounts of major and trace elements which can be introduced from silicate rock materials during a standard acid extraction procedure can vary within very wide limits. Even if the experimental conditions of these studies are not identical, the results are unambiguous and give the same general conclusions on solubility.

The contributions of analyte elements from the geological material used as the medium may, in extreme cases, disturb or even overshadow effects which are to be studied; the danger being especially great when working at low concentration levels and with marginal effects. A stable background contribution from the medium is important and requires that the medium is homogeneous. This can be a problem for many sediments, which often are inhomogeneous due to mineral segregations.

Analytically, the ICP-AES technique is sensitive to high contents of dissolved solids, and problems like clogging of the nebulizer and build up of solids on the tip of the torch are well known. Line interferences and interelement corrections create additional problems which often seriously degrade analytical quality. These problems must be taken into account when the total analytical procedure is to be considered.

The use of reference materials is a central element in quality control. However, such materials are normally certified for total element content, and are therefore of limited value for extraction analyses. The best alternative in such cases will be to base the control on inter-laboratory comparisons, and where identical and reproducible extraction procedures are being used.

The main intention of this work has been to focus on some of the many problems and pitfalls which can be encountered in geochemical and environmental studies based on geological materials, and the few examples outlined show that such activity requires multiprofessional knowledge at all stages from planning to the final interpretation.

Systematic research on the general solubility of rock-forming silicate minerals has been of particular significance in this field, and has contributed considerably towards providing a safer basis for drawing conclusions.

References

[1] Graff, P. R. & Røste, J. R. 1985: Utluting av silikatmineraler med mineralsyrer. Nor. geol. unders. Report 85.105, 26 pp.

[2] Faye, G. Chr. 1982: Metodestudier i geokjemi - HNO_3-ekstraksjon av geokjemiske prøver. Nor. geol. unders. Report 1687 C, 19 pp.

[3] Gautneb, H & Bakken, A. K. 1995: Crushed rocks, minerals and mine tailings as sources of potassium in agriculture. Nor. geol. unders. Bull. 427, 4 pp.

[4] IKU A/S, Continental Shelf and Petroleum Technology Research Institute A/S 1988e: Statfjord environmental survey 1987. Report no. 02.0840, 134 pp.

[5] Ødegård, M. 1981: The use of inductively coupled argon plasma atomic emission spectroscopy in the analysis of stream sediments. J. Geochem. Explor.14, 119-130.