ANALYSIS OF GEOLOGICAL MATERIALS BY ICP-AES IN DEPARTMENT OF GEOLOGY, SAINT-ETIENNE SCHOOL OF MINES

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NOTICE

This document is an internal report, intending to inform, on the most practical point of view, about

* the equipment used in our laboratory for ICP analysis of materials;

* the procedures used for sample preparation;

* the separation schemes used for some trace elements (especially REE, procedures under study for Th, Nb-Ta ...);

* [under reconstruction: the main spectral interferences found with the analytical lines used].

This document is not intended for ICP spectroscopists and skilled analysts; it deals with very common problems encountered by geologists using ICP in a do-it-yourself way, which is (supposed to be) the case in our laboratory.

INTRODUCTION

Inductively-Coupled-Plasma-Atomic-Emission-Spectrometry has been installed in our laboratory in Feb.1985. As the routine analysis of major and trace elements in rocks is usually done here by XRF-spectrometry (Philips PW1404), we use ICP-AES mainly as a complementary tool for :

a/ analysis of trace elements in rocks:

> * Li, Be (too light for detection by XRF),

> * REE (only La, Ce, Y are analysed by XRF),

> * Sc-V-Cr-Co (not analysed here by XRF, because we calculate the background with the Compton peak method) ;

b/ analysis of major and trace element in mineral separates (too much material is needed for XRF analysis of trace elements) ;

c/ replicate analysis of elements already analysed by XRF : for example for precise determination of Ti, Mn, Mg... at low level, analysis of Na (sometimes problematic by XRF)...

It is mainly for practical reasons, due to organization constraints in our laboratory, that routine analysis is made by XRF and not by ICP. I think that, when correctly used, and especially when using a polychromator, ICP-AES may also be very powerful for rapid, precise, and low-cost determination of major as well as most trace elements (with the noticeable exception of Rb and Cs, which could be analysed from the same solution by flame emission).

An analytical equipment for ICP - atomic emission spectrometry basically comprises two main parts :

* the source, which is composed of the ICP-torch, its HF generator, nebulisation system, etc...

* the optical system used to analyse the light emitted by the analyte solution passing through the torch.

A short History : Our first system, in 1985, was a Jobin Yvon JY38VHR, which comprises a scanning monochromator ; to this system was added, in 1987, a polychromator (JY32, with 20 analytical lines, extended later to 37 lines). The system worked was updated in 1990 : modification in the electronics, the computer (from apple ii to PC), in the motor of monochromator grating, etc. Then, as the manual operation of the 'torch' was considered as uncomfortable by our colleagues of the Physical Chemistry Dept, we buy a new system, the JY138 Ultrace.

POLYCHROMATOR SYSTEM : JY32

The system, manufactured by Jobin-Yvon (Longjumeau, France) contains the following units :

HF GENERATOR (JY32)

Durr-JY 3832; frequency: 56MHz; Power output: 2300W; auto-tuned; generally operated at the lowermost power (4.2 kV, 0.38 A, 130 mA). The high frequency (as compared with the 27.12 MHz used by many makers, particularly in USA and Japan) is known to improve the signal-to-background ratio, because, whereas electron density and excitation temperature decrease with increasing frequency, the argon continuum decreases as the square of the frequency (JY Mermet, passim).

TORCH (JY32)

5-turn induction coil; demountable torch (INSA patent, consists of 2 quartz tubes and an alumina injector mounted on metallic holder) ; operated with a main plasma flow (so-called "coolant") of 12 to 14 l/min (may vary according to modifications in the configuration of the tubes); argon sheath system (Ar 0.35 l/min, and 1.2 for determination of trace of alkali metals): before introduction in the plasma through the injector, the aerosol is sheathed with argon. This argon sheath prevents the aerosol to contact the walls of the injector tube. It is also used to control the parameters of the discharge (temperature, residence time), and this proves especially useful for the determination of alkali metals (switching from high to low flow-rate is computer-controlled).

POLYCHROMATOR OPTICS

the JY32 includes two optical elements:

* main polychromator :
>Paschen-Runge configuration, 0.5 meter focal length ;
>concave holographic grating, 3600 r/mm, linear dispersion 0.55 nm/mm (1st order) ;
>spectral range 170-410 nm ;

* additional polychromator, for the determination of alkali elements (Li, Na, K) : flat-field grating, 1200 r/mm holographic grating, spectral

range 400-900 nm.

The entrance slit is 0.040 mm large, the exit slits are 0.040 to 0.050 mm large ; the entrance slit is motorized and its position is computer-controlled, this enables background measurements during routine analysis, and scanning for the study of interferences.

ELECTRONICS (JY32)

In the original equipment, the electronics that controls
>   the photo-multipliers of both spectrometers,
>   the motor of the monochromator grating,
>   the motor of the polychromator entrance slit

are connected to three A/D cards contained in the Apple microcomputer. This configuration has been modified afterwards, and now, in the two spectrometers we have, all the electronics, including A/D conversion, are contained in a single "Spectralink" box, which is connected directly to the RS232 series port of the microcomputer. The same software library may be used on the JY32 and the JY138.

COMPUTER (JY32)

The HF Generator and the torch are manually operated : this part of the system does not need modification during analysis. At the beginning, the spectrometers were controlled by an Apple IIe microcomputer (64Kb RAM, two 143Kb / 5'25 floppy-disks) which was then replaced by an Apple II GS (512Kb RAM - 256Kb used as RAM disk -, one 800Kb / 3'5 floppy disk), and, in 1990, by a PC-compatible machine, together with an upgrading of the scanning spectrometer itself.

It may be mentioned that, although the computer capacities were enormously increased (for example, from 64 Kbyte to 16,000 Kb of RAM, and from 0.143 Mbyte to 512 Mb of mass memory), the program distributed by Jobin-Yvon remains basically the same.

The microcomputer controls

* the step motor that controls the grating position of the monochromator (one step unit = 0.0013 nm),

* the voltage applied to the photomultiplier of the monochromator,

* the step motor that controls the position of the polychromator entrance slit.

It controls the measure parameters (measurement times) and reads the signals on the photomultipliers. The Apple II was operated under UCSD Pascal (Apple Pascal) system. The PC operates under MS-DOS.

Of course, the equipment comes with a complete software that controls all the analytical tasks and performs the complete analytical cycle, including treatment of spectral interferences. However, we have found more convenient to write our own software that controls the main analytical tasks. As the basic operations are controlled by routines in 6502 assembly language, supplied with the equipment, it has been easy, with a minimum knowledge of Pascal programming and of the UCSD operating system, to link these routines to Pascal programs, in order to write our own program directly in Pascal.

Actually, the AppleII performed only the data acquisition : the raw data were only saved as text files on the Apple floppy disk during analysis, and then, after completion of a series of analysis, they were transmitted, through the RS232 port, to an IBM-PC-compatible machine, which performed the data correction.

We preferred this method for several reasons:

* processing of geochemical data is made, in our lab, on IBM-compatible machines,

* Apple II is a relatively old machine, with a slow microprocessor, it has too small RAM and too limited mass memory for the processing of large data files and its UCSD system does not support MS-DOS like tree organization of file directories, which is very convenient for handling large data bases. As already mentioned, the new generation of JY spectrometers may be controlled directly by PC/XT or AT machines, and this has allowed a much more extensive exploitation of the spectral data, especially with the monochromator.

nebuliser

Meinhard (type C) concentric nebuliser;

operated at 2.8 to 3.2 bar, with 0.30 l/min Ar (as read on a flow-meter under 2.75 bar);

solution uptake rate:

free running : 0.8 ml/min [generally increasing with the age of the nebulosity : may reach 1 ml/mn after a few months of operation]

with pump : 0.8 - 1.0 ml/min.

to prevent clogging by highly salted solution, nebulisation argon first passes through an 'argon humidifier' (Jobin-Yvon patent).

this nebuliser has been used for years with a Scott-type nebulisation chamber, and from 1995 with a cyclone-type chamber.

The nebuliser has been used 'free running' for many years, because the samples were managed manually : it is important in this case to minimize the time between the introduction of the capillary in the sample and the stabilization of the nebulisation system. A depollution delay of about 20 seconds was obtained with a short length of capillary from solution to nebuliser. Also, the peristaltic pump is not necessary here because we are analysing solution of very low and constant viscosity.

However, when we began to use an automatic sampler (a Gilson 222, controlled through a RS232 series interface, with specific routines, written in Pascal), it was necessary to use a peristaltic pump, because of the longer length of tubing. The pump is a Gilson Minipuls 3, which is interfaced with the sampler : the Gilson software controls controls also the pump (on/ off, rotation speed, etc.). Using an auto-sampler and a peristaltic pump induces a large dead volume of tubing, which is taken into account by our program (see below).

After several years of operation without problems, and with relatively low operating costs (one nebuliser every 2000 to 3000 analyses), we are using a somewhat different nebulisation system : it is also based on a quartz-made concentric nebuliser (Australian-made, somewhat cheaper than a 'true' Meinhard), but the nebulisation chamber, instead of the classical Scott-type, is of the Cyclon-type (the nebulisate is introduced tangentially instead of centrally). It seems that this change resulted in a signal being about 20 % higher than with the Meinhard/ Scott

combination.

Other nebulisers have been used :

> Jobin-Yvon concentric nebuliser,
> cross-flow nebuliser,
> MCN concentric nebuliser,

but none of them gave significantly better results than the Meinhard-type nebulisers. The only problem is thus the analysis of aggressive solutions (namely, HF-bearing solutions).

Note concerning the Auto Sampler :

The auto sampler is a Gilson 222 sampler, that allows direct access of the x, y, z coordinates of the position of the needle connected to the tubing to the nebuliser. Compared to purely sequential sampler, this X-Y sampler makes it possible to access directly to predefined positions : for example, we program the analysis of a series of 5 samples [separated by a quick return of the needle tip to a washing solution (2 seconds)], which is followed by a direct access to definite position of the blank solution and then to the control solution, and so on.

In that case, the dead volume represented by the capillary is longer than in the manual operation, but our program allows to change sample before the analysis of the current sample has been finished : the solution remaining in the capillary after changing sample position is used for the last thirty seconds of the analytical cycle. Doing so, a complete analytical cycle, including complete depollution, lasts only 55 seconds. Of course, this is made possible by a personal programming of the routines controlling the spectrometer and the sampler, all furnished as Pascal libraries by Jobin-Yvon and by Gilson, and I am not sure that this trick is available on commercial apparatus with closed software.

SCANNING MONOCHROMATOR : JY138 Ultrace

Czerny-Turner configuration; 1 meter focal length;
blazed holographic (master) grating 2400 rules/mm, 120 by 140 mm;
theoretical resolution: 504000 ; linear dispersion : 0.266 nm/mm (1st order);
Used in the second order up to 310 nm.
programmable slits : entrance slit 10 / 20 um; exit slit 15 / 77 um.

Generally, we use the following entrance/ exit slit combinations :

> 20/15 when high resolution is needed, i.e. for trace elements,
> 20/77 when high precision in the measure of the peak height is needed (e.g. for major elements).

SAMPLE PREPARATION

Sample preparation is a critical step in the application of ICP-AES to geochemistry.

Also decisive, before dissolution, is the grinding technique : of course, better results are obtained (esp. with acid digestion of refractory minerals, e.g. zircon) when the sample has been very finely ground in a non-polluting device. Here, not only the grain is critical : it is also important, if

possible, to use agate or corindon and not to use steel or tungsten carbide in the grinding stage, because ICP-AES is an efficient method for the determination of low amounts of transition metals Cr, Co, Ni, etc., and these elements, which may be of great petrological interest, are prone to pollution by such grinding material.

Our grinding procedure is as follows:

1. break the sample, with a hammer or a guillotine, into pieces <2 cm;

2. crush, in a jaw-crusher (iron jaws), to diameter less than 5 mm; [at this stage of the procedure, using iron, if it is relatively soft, is not critical];

3. take a representative sample of the crushed materiel and grind it for 12 to 16 minutes using an agate ring-grinder.

We use several kinds of procedures for the dissolution of geological samples:

* the most commonly used is a multi acid (HCl/HNO3/HF) digestion;
* for exploration geochemistry of gold-related metals (sulphide-bound metals, especially As, Sb...), we use aqua regia digestion at relatively low temperature;
* in some cases, for the analysis of samples that cannot be managed with the XRF, we use alkaline (LiBO2) fusion.

MULTIACID DIGESTION

Equipment :

* electronic balance Sartorius 1801, precision 0.1 mg, 0-160 g ;
* electronic balance Sartorius 1400, precision 0.1 g, 0-2200 g ;
* fume hood, and fume evacuation system, all polypropylene ;
* hot plate 2200W (0 - 200°C), power input controlled by a triac (outside the fume cupboard) and a timer 0-24 Hour ;
* aluminium blocks, each with 10 holes 32 mm diameter, to receive the Teflon vessels ;
* 100 Teflon vessels, 30 mm external diametre., 30 ml, with screw caps, from Savillex (Minnesota, USA) ;
* acid dispensers 0-10 ml.

The methods described here are similar to those used in most laboratories. The only difference with more classic methods lies in the use of PTFE vessels equipped with Teflon screw cap : although they are not really digestion bombs, they allow some pressure to build up during heating, they insure more efficient digestion of refractory minerals (tourmaline, cassiterite) and they reduce the amount of acid required for dissolution.

Another peculiarity of the method is that we do not use volumetric flasks, thanks to the availability of precise electronic balances at relatively low cost.

For the heating of the closed vessels, microwave oven can be used, it is much quicker and efficient than hot plate, but, as we are using common equipment for cooking (10 times cheaper than the oven designed for laboratory equipment), the vessels are not put directly into the oven (in the case of overpressure and leaking of the vessels, acid fumes would very soon damage the magnetron) but into a polystyrene vacuum dessicator. As

the temperature cannot be measured during experiment, input power and digestion times have to be estimated beforehand with the vessels filled with water. Note that the heating parameters (time and power) depend on the total amount of solution in the oven (i.e. number of vessels and amount of solution in each one). Steps 3 and 5 may thus be replaced by repeated heating, of 3 to 5 minutes each, at 500 W.

Complete removal of excess HF, in step 4, is critical for ICP, because the presence of traces of HF in the solution rapidly damage the Meinhard nebuliser (which is not cheap) ; note that the so-called "neutralization of excess HF with boric acid", a technique sometimes used in AAS, has not proved efficient enough in ICP (cf. Thompson and Walsh, 1984).

The removal of excess HF is usually done by taking into dryness the HF-bearing solution in presence of an acid with high-boiling point, usually $HClO_4$. To avoid using $HClO_4$, H_2SO_4 is used in some labs, but this acid is very long to boil out, especially the Teflon containers cannot be used at high temperatures, and the resulting sulphates are often difficult to redissolve. So we choose to replace $HClO_4$ by repeatedly drying HF in presence of excess HNO_3 and then HCl. No damage of the nebuliser was observed with these solutions.

1. Weigh about 300mg of sample (very finely ground) into a 30ml PTFE vessel ;

2. Add 1 ml 10M HNO_3 and 3ml 10M HCl; put the OPEN vessel into aluminium blocks on a hot plate at 110 C; heat until incipient dryness (2 - 3 hours) ;

3. Add 3ml 29N HF, CLOSE the vessels tight and heat at 110 C for 16 hours (overnight) ;

4. Let cool, OPEN the vessels, heat at 160 C until dry (3 hours) ;

5. Let cool, add 3 ml 10M HNO_3, heat at 110 C until dry (3 hours) ;

6. Add 3 ml 10M HNO_3, heat at 110 C until dry (3 hours) ;

7. Add 3 ml 10M HCl, heat at 110 C until dry (3 hours) ;

8. Add 4ml 2M HCl and 10ml DeIonised water, CLOSE the vessels, heat for 2 hours at 110 C to redissolve the salts ;

9. Transfer to polystyrene tubes previously weighted on an electronic balance, and make, with D.I. water, to 50 times the initial weight ;

10. To clean the vessels, fill with 10ml 2M HNO_3, close the vessels, and heat at 110 C for 4 hours, and then open, rinse with D.I. water, and dry the vessels.

Although this procedure takes about three days, it is possible, using a large number of Teflon vessels (which cost about US$ 10 each, and last several years if not overheated), to prepare many samples (up to 100, depending on the size of the hot plate and the fume hood) in a same batch. Using electronic balance instead of volumetric flasks for step 9 saves much time and money, and may be integrated, in the future, in an robotised procedure.

Having purchased a comfortable number of Teflon beakers, and having registered, in a spreadsheet file, the weights of each beaker, and of its cap, we simplified the steps 7 and 8 as follows :

* A stock of 2M HCL being prepared separately in a bottle equipped with a dispenser, about 25 ml is poured in each Teflon beaker, the beakers are closed, and heated a few hours on a hot plate at 110 C.

* Before analysing the solution (directly from the beaker), the beakers are weighted, the weights are input on the spreadsheet containing the sample list, and the precise dilution ratio is computed.

* After analysis, our data reduction program will find directly, from the sample list file, the correspondence between solution number, sample name, and dilution ratio.

Pro's and Contra's of the Acid Method

After having processed about 20,000 samples with these procedures, we can say that, the main ADVANTAGES of the acid dissolution procedures are :

1. its simplicity ;

2. the low cost of the equipment required ;

3. the low levels of blank solution obtained: high-purity acids are readily available on the market; actually, we found no significant difference in trace elements between the blank solutions included in each batch and a simple HCl 2M solution ;

4. the low dilution ratio (sample weight / solution weight), which allows most elements to be readily analysed, down to the ppm level, without chemical separation ;

5. the low salt content of the solution, which is a critical parameter, both for an efficient and stable nebulisation and for the emission processes occurring in the plasma.

On the other hand, the main PITFALLS of the acid dissolution are:

<1>. Some minerals are known to be relatively resistant: they are mainly zircon, kyanite, chromite; this is especially important for analysis of REE in granitic and sedimentary rocks, because zircon may contain an important part of the REE stock (and particularly heavy REE) of the rock.

Complete dissolution of these minerals could be obtained either

 by acid dissolution at higher temperature in Teflon/steel high-pressure bombs (cf methods used by isotope geochemists),

 or by 'mini-fusion' method (filtering the solution, alkaline fusion of the filtrate),

 or by an alkaline fusion (cf infra).

 However, with our method, if the finely ground powder is heated at about 150°C for two days with HF, we observe on many geostandard samples an almost complete recovery or Zr and Cr.

<2>. Some elements are lost by evaporation: this is the case, definitely, for Si and B; other elements (Sn, Mo, many metalloids like As, Sb,...) are

said to be lost during fuming HF off in presence of HClO4. Comparing results with those obtained by low temperature (100°C) aqua regia digestion, we have observed loss of As.

Evaporation of Si as a fluoride (H2SiF6 ?) is not an important problem in our case, because major elements are analysed separately, in our laboratory, by XRF. Moreover, considering that SiO2 constitutes 40 to 80 weight % of most silicate samples, evaporation of Si presents the advantage of drastically reduce the total salt content of the solution and to allow thus a low sample/solution ratio to be used.

<3>. The low sample/solution ratio chosen here for the acid procedure leads to low detection limits for trace elements, but it leads also to some difficulty in the accurate analysis of major elements. ICP-AES is known for the very large concentration domain within which the light intensity emitted on a given analytical line remains proportional to the elemental concentration. This linearity domain extends up to about 10^5 times the detection limit : this corresponds to about 100 ppm in solution for highly emissive elements (such as Mg, Ca, Ti...), and to about 5000 ppm for less emissive elements (Al, Na, K...). Above these limits, the calibration curve (i.e. the curve giving the emission 'signal' as a function of the concentration) shows a curvature that is not easy to quantify accurately; in that case, it may be more accurate, considering the rapidity of analysis with a polychromator, to analyse the solutions two times: a first time for trace and minor elements, a second time, for major elements, after a 10- to 50-fold dilution with 2M HCl.

ALKALINE FUSION

In order to eliminate most of the shortcomings of the acid procedure, we implemented also a sample preparation procedure by alkaline fusion.

The procedure used is as follows :

1. Put 500 mg of LiBO2 and 100 mg of finely ground sample in a carbon crucible, mix thoroughly ; [actually, a better mixing of flux and sample is obtained by weighing in a separate glass beaker, mixing, and pouring into the crucible]

2. Melt the mixture in a muffle furnace (30 minutes at 1050 C, put as many samples as your stirring device will accept) or in an induction furnace (5 minutes) ;

3. Pour the melt directly, as quick as possible, into a Teflon beaker containing about 50 ml 2M HNO3, and let it dissolve on a magnetic stirring device for about one hour at room temperature ; complete dissolution is generally obtained within 15 to 30 minutes ;

4. Complete the solution at 50 g with 2M HNO3.

5. Pass the solution through a paper filter, in order to remove the carbon particles, and store in polystyrene tube for analysis.

[Here also, using an electronic balance for the dilution step saves time, and it is probably as precise as using volumetric flasks]

The solution will thus contain 12 g/litre of salt, and correspond to a sample/solution ratio of 1:500.

Note that dilution of the melt in dilute HCl instead of HNO3 in step 3 generally leads to solutions that may turn very viscous in a few days (formation of silica gels) and cannot be nebulised. However, in the method used in the C.R.P.G. (a CNRS laboratory in Nancy with a very long experience of ICP in geochemistry), a 'complexing solution' (mainly dilute HCl with oxalic acid and H2O2) is used for the dilution (the role of the

complexing agent is actually for subsequent REE separation).

Note: fully automated (microprocessor-controlled) machines, originally designed for processing fusion samples for XRF, are available, but they are much more expensive than the equipment for manual operation with a muffle furnace, and, moreover, they are not as efficient, for several reasons :

the delay between end of fusion and pouring the melt in the acid is too long,
and the crucible is too high, so that some melt is left in the crucible ...
the samples are processed one by one, and not by batches as in a muffle furnace: the productivity is not increased;
they generally use expensive glassy carbon crucibles (instead of small and cheap graphite crucibles);

Although we have not used this procedure for routine analysis of many samples, we can say, from our experience on geostandards, that the main **ADVANTAGES** of the alkaline fusion procedure are :

* most minerals, including chromite, zircon, etc. are melted and dissolved;* it is a rather simple method;

* silica can be analysed, and thus, as all the major elements are measured, the consistency of the analysis can be controlled by computing the total of the oxides, provided that the sample is oven-dried beforehand or that the loss on ignition has been determined;

* moreover, as the sample/solution ratio is much lower than in the acid method, the calibration curves do not show any curvature, even for most emissive elements (Ca, Mg), and the data correction is thus simplified.

* The alkaline flux plays also a role of buffer that prevents possible matrix effect. Although the ICP method, thanks to the very high temperature of the source, is renowned for the absence of the 'chemical interferences' [which are well known in lower temperature sources like flames or microwave plasmas], matrix effects may be sometimes observed, for example for aluminium: we observe for example, in solutions made from geostandards with the acid methods, that the calibration curve of Al has not exactly the same slope in granitic rocks and in basaltic rocks.

The main **PITFALLS** of the alkaline fusion procedure are:

* the sample/solution ratio is much higher than in the acid procedure, so the detection limits are 5 to 10 times higher ; many elements become difficult to analyse without chemical separation ;

* the salt content of the solution is higher, this may have some influence on nebulisation and stability of the torch ;

* Li and B cannot be measured, unless another flux (Na_2CO_3, KHF_2...) is used, but it will generally contain an alkali metal ;

* whereas it is easy to find high-purity acids at relatively low cost, alkaline fluxes are generally less pure and the blank levels are not so low (some fluxes are very high in La, and really pure fluxes are not cheap).

In conclusion, the best method to obtain reliable results on both major and trace elements appears to use concurrently the two methods : the acid dissolution for most minor and trace elements, and the alkaline fusion for major element determination and to check the dissolution of zircon and the determination of Zr, Y, REE,... For a given series of rocks, the two series of solution obtained must be analysed as two completely separated sequences, with the acid series preceding the alkaline one, because it takes some time for a complete cleaning of Li in the nebulisation

system.

For laboratories using both XRF and ICP-AES, major element determination would be made with XRF, so that ICP-AES is used for trace and rare earth element determination on solutions made mainly with acid dissolution procedures.

METHODS OF SEPARATION

On most types of rocks, Y, La, Ce, Eu, Yb can be readily determined, without separation, on the solution obtained by the acid method, down to about ten times the chondritic abundances.

Other rare earth elements (Nd, Dy) may also be determined accurately if the rock is poor in Ti, Fe, Mn, ... for example in granites, aplites, pegmatites, or in siliceous sediments.

However, a precise analysis of REE spectra, including the middle REE (Sm, Gd) is generally only possible when the REE have been isolated from the main interfering elements, especially Ti, Fe, Mn, Zr (cf. section 5). In that case, REE can be analysed down to the chondritic abundances.

The procedure used for the separation of REE from major and most trace elements is derived from chromatographic methods already described by many authors (see review in Thomson and Walsh). The main difference lies in the small size of the columns used, and thus the small amounts of acid required for the different elution steps, and, as a consequence, the lower levels of the blank solution and the shorter time of the procedure.

Equipment and Products

The chromatography columns are small polypropylene columns PolyPrep from BioRad (Dow Chemical); reservoir for resin bed = 2.5 ml; reservoir for eluting solution = 11 ml.

The resin is the strongly cationic ion-exchange resin, Dowex AG-50-W-X8, 200-400 mesh, from BioRad ('AG' stands for 'Analytical Grade', which differs from common grade resins by a sharper distribution of the grain size).

Procedures:

We used successively two procedures, which we will comment here briefly.

A procedure of cation-exchange chromatography basically consists of the following steps:

1. equilibrate the resin with the acid normality of the sample ;

2. charge the sample solution on the resin ;

3. elute the elements to be eliminated ;

4. elute the REE (and simultaneously clean the resin).

The elution procedures can be easily tested, on solutions made from different types of rocks (granite, basalt,...), by branching the column,

through a peristaltic pump, to the input of the nebuliser of the ICP, and by integrating the intensities obtained on the polychromator every 30 seconds. It is thus possible to obtain a series of chromatograms in a very short time, in order to adjust the volumes of the eluting solutions, and to insure the following requirements :

1. no REE appears in the eluate at the end of step 3 (especially the heavy REE, which have the lowest resin/solution partition coefficient in HCl conditions) ;

actually the chromatograms show that Mg, Ca, Sr, and Ba are, in that order, the last major elements eluted in step 3.

2. the exchange capacity of the resin is not saturated (in which case REE could be lost) ;

3. elution volume in step 4 is sufficient to insure complete removal of the REE from the column.

The equilibrium partition coefficients (= [conc. in the resin] / [conc. in the solution]) have been published by Strelow and co-workers for most elements and for different types of acid (HCl, HNO3, HCl-oxalic acid,...). From these data, it can be inferred (and that is confirmed by experiments by Crock et al. and by our own chromatograms) that there is a strong fractionation among REE in HCl conditions, and consequently a long tailing has been observed on La and Ce chromatograms when HCl is used on step 4, whereas all REE are more quickly and simultaneously eluted with HNO3 solution. However, if HNO3 is used from the beginning, Fe III is retained on the column, whereas, in HCl solutions, it behaves as Fe II and is eluted with other major elements.

For these reasons, we use successively HCl and then HNO3 (with a rinsing step with H2O that separate HCl solutions from HNO3 solutions : the chromatograms have shown that no element is detected during this rinsing step).

PROCEDURE A FOR REE SEPARATION

1. The columns are filled with 2.5 ml of wet resin ;

2. EQUILIBRATION: fill the the reservoir with 10 ml HCl 2M ;

3. CHARGE 8 ml of the analyte solution ;

4. Elute the MAJOR elements by filling the reservoir with 5 ml HCl 2M ;

5. RINSE the resin with 5 ml D.I. H2O ;

6. Elute the RARE EARTH Elements with 10 ml HNO3 5M ;

7. RINSE the resin with 10 ml D.I. H2O.

All the eluting solutions produced in step 2 to 5 are discarded. The eluate of step 5 is taken into a PFA beaker and taken to dryness on a hot plate at 110 C, and the residue is then taken in 2.5 ml HCl 2M, to be analysed by ICP.

PROCEDURE B FOR REE SEPARATION

This separation procedure for REE has been modified following the publication by Govindaraju and Mevelle of the procedure used by CRPG (Nancy, France), which has a long experience of REE separation for ICP analysis. The difference with procedure A is that, before charging on the column, 4 ml of the sample solution is mixed with 4 ml of a 'complexing solution' consisting of $(HCOOH)_2$ (50 g/kg) and H_2O_2 (25 ml/kg). In that case, as shown by the systematic studies by Strelow and co-workers, the major elements are mostly transformed to anionic or neutral complexes and are not retained on the resin. This prevents from saturation of the resin by these elements, and, as Fe is already washed out on step 1, HNO_3 can be used for Ca-Mg-Sr-Ba elution.

The procedure is thus as follows:

1. The columns are filled with 2.5 ml of wet resin ;

2. EQUILIBRATION : fill the the reservoir with 10 ml HCl 2M ;

3. CHARGE 4 ml of sample solution mixed with 4 ml of complexing solution ;

4. RINSE the resin with 5 ml D.I. H_2O ;

5. Elute the remaining Ca-Mg 2 ml HNO_3 2M ;

6. Elute the RARE EARTH Elements with 10 ml HNO_3 5M ;

7. RINSE the resin with 10 ml D.I. H_2O.

SAMPLE ANALYSIS

As said before, we completely separate the data acquisition procedure from the subsequent step of data correction : the data acquisition procedure will produce only raw spectrometric data on the different types of solutions (calibration, stability control, unknown samples), then, in the data correction procedure, the spectrometric data are converted to analytical results.

This differs from the 'normal' procedures of commercial software, which produce generally on-line data correction. In our system, the raw data (peak, background, etc., on both unknown and standard) are acquired, and subsequently, after completion of the complete series of measurements, they are corrected and adjusted.

Although the ICP system allows data acquisition on both monochromator and polychromator optics in the same analytical cycle, we generally use the two optics successively, in two analytical cycles. The two kind of optics have different performances :

1. the polychromator is quick (one minute per sample), and, due to relatively long integration times (generally 5 seconds, repeated 3 times), it gives precise measurements ;

2. the monochromator is much slower (about 3 minutes for the analysis for 10 elements in one sample), has a lower reproducibility (each scan step is measured for only 0.400 to 0.800 second), but its resolution power is twice that of the polychromator (or even better with the 138), and it

can be used for a detailed analysis of a given line and its background.

As a consequence, the polychromator is used for systematic analysis of large batches of samples (up to 400 per day), whereas the monochromator is used as a complementary tool for the precise determination of some trace elements in some selected samples.

Data Acquisition with the Polychromator

Each measure is composed of

* 30 sec. of depollution ;
* 5 sec. integration on Left Background position ;
* 3 times 5 sec. integration Peak position ;
* 5 sec. integration on Right Background position.

All the data are stored on the hard disk.

The acquisition of spectrometric data of a series of unknown samples typically comprises the following steps organized as loops :

Step 1 : OPTIMIZE THE ENTRANCE SLIT POSITION
Step 2 : UPDATE THE INTERFERENCE COEFFICIENTS
Step 3 : MEASURE SYNTHETIC CONTROL SAMPLE(S)
Step 4 : (MEASURE GEOSTANDARD SAMPLES)
(Step 5 : UPDATE CURVATURE COEFFICIENTS)
MEASURE UNKNOWN SAMPLES (10 to 20)

Step 1 OPTIMIZE THE ENTRANCE SLIT POSITION

Just after 'lighting' the plasma, during the time required for the stabilization of the source (about 30 minutes), the polychromator is optically adjusted : a multi-element synthetic solution is nebulised, and a program is used to find which position of the entrance slit gives a maximum signal on most of the elements. This is done only once in the day.

Step 2 UPDATE THE INTERFERENCE COEFFICIENTS

Even if the scanning profiles have already been investigated in detail in the preliminary interference studies, interference coefficients for the major and minor most interfering elements (Ti,Fe,Mn,Mg,Sr,Zr,V) have to be updated, because even small variations in these coefficients introduce significant errors on the determination of the interfered elements. These coefficients are not intrinsic : they depend on many parameters (torch parameters, observation height, entrance slit position,...). This updating has to be made each time the parameters of the source are modified.

Step 3 MEASURE SYNTHETIC CONTROL SAMPLE(S)

In the case of solutions obtained by acid decomposition, the low dilution ratio (sample / solution) leads to curved calibration lines for the most emissive elements. In order to quantify these curvatures, a series of synthetic multi-element (Ti-Al-Fe-Mn-Mg-Ca) solutions representing increasing concentrations (100 / 200 / 400/ 800 / 1000 ppm) may be analysed. These data will be used to update the curvature coefficients used by the correction program. However, as we use ICP as a complementary tool, this step is generally not necessary.

Step 4 (MEASURE GEOSTANDARD SAMPLES)

In ICP, the calculation of the elemental concentrations in the samples is made by direct comparison with the emissions measured on reference samples. These are international reference materials obtained from geochemical laboratories (USGS, GSJ, CRPG...), which we progressively replace with our own reference samples. These samples are only analysed once in a series of analyses ; otherwise, the correction of instrumental drift during the course of the analysis is done by measuring two synthetic reference samples :

* one represents the 'zero' of the calibration curve : it is either the 2M HCl solution used for acid decomposition, or the LiBO2 flux decomposed in the 2M HNO3 acid used for alkaline fusion. An accurate determination of these samples is essential for a good determination of trace elements.

* the other will be used as the second point of the calibration line. It is obtained by mixing accurately (easily done on an electronic balance) different stock solutions containing known concentrations of the elements to be analysed.

The following stock solutions are used (concentrations in ppm) :

a. Major elements :

> Al+Fe+Mg+Ca+Na+K:2000 each
> + Ti:400
> + Mn:200
> + Li:20 ;

b. Sr-Ba-Zr : Sr200+Ba200+Zr100 ;

c: Transition elements : Sc10+V+Cr+Co+Ni+Cu+Zn: 100 each;

d: REE : La,Ce,Nd:100; Sm,Gd,Dy,Er: 50; Eu,Yb,Y: 10;

e: Nb-Ta-Be-Th : Nb,Ta,Th:50;Be:10.

These solutions are mixed in the proportions a:b:c:d:e = 5:1:2:1:1.

As the source we are using is relatively stable, reproducibility better than 1 % is obtained when measuring these two control samples every ten samples (about 10 minutes) during the first hour of plasma, and every 20 samples afterwards.

Data Correction with the Polychromator

The conversion of the spectrometric data to elemental concentrations comprise the following steps :

* using the data on control samples, convert all data to ppm in solution relatively to the 'theoretical' concentrations of the control sample (as the control sample contain major as well as trace elements, the concentrations of interfered elements must have been recalculated using the table of interference coefficients) ;

* the results of these calculations on the interference mono-elementary solutions are used to update the matrix of interference coefficients (note that these coefficients are calculated BEFORE any curvature correction for major elements) ;

* using the new table of interference coefficients, the concentrations computed in a/ are corrected for eventual interferences. For this we suppose a linear relation, and the correction instruction is thus, for the concentration ppm[i] of the trace i in the sample,

ppm[i]:= ppm[i] - sum_on_j_of(ppm[j] * interf_coef[j,i]),

where interf_coef[j,i] is the interference coefficient of element j on element i. Here also, the interference is calculated according to the 'theoretical' values of ppm[j], before curvature correction. In the case of cross-interferences (for example between Ce and Nd), the interference correction must be looped.

* the results of step a/ on the solutions for curvature estimation are used to update the curvature coefficients of major elements; after trying different analytical formulations of correction functions, we finally decided that the safest way to express these curvatures as a set of coefficients is simply to divide the calibration curve in a series of straight lines... Although not very sophisticated, this kind of treatment has proved to give good results, whereas polynomial approximation of the calibration lines may lead to large errors.

Anyway, as already mentioned, when a precise analysis of major elements is needed, the best results appear to be obtained on less concentrated solutions.

Using the curvature coefficients computed in d/ or the default coefficients previously saved on a file, the major elements are corrected for eventual curvatures.

* after correction for the dilution ratio, the results obtained on the reference samples are compared, using an interactive graphic program, to their recommended values.

Data Acquisition with the Scanning Monochromator

Compared with the polychromator, there are some differences in the sequence of data acquisition with the monochromator, because of some peculiarities of the system.

As the focal length is twice that of the polychromator, the spectrometer is subject to mechanical drifting. The control solution, that contains all the elements to be analysed, is measured every ten minutes in order to update the instrumental positions of the analytical lines. The intensities are also used to correct the instrumental drift of the source, in the same way as for the polychromator.

An analytical series comprises the following steps :

<1>. select the analytical lines from the line library, which contains, for each element, one or several lines, each with :

* its theoretical wavelength,
* the last value of the corresponding practical wavelength position,
* the relative position for background measurement,
* the integration time (generally 0.400 seconds, 0.800 for W, Mo, Ta).

<2>. search for the actual peak position of each line.

<3>. measure successively :

* blank solution,
* control solution,
* mono-element solutions of potentially interfering elements.

<4>. measure successively :

* blank solution,
* control solution,
* unknown samples.

<5>. repeat cycle 4 ad lib.

For each measure, the spectrometer scan each line, successively, in order of increasing wavelength. The scanning step is 0.00133 nm large. Each line is scanned, around the peak position, for

* 5 steps for the unknown samples ;

* 3 steps for the blank sample ;

* 9 steps for the control sample.

After completion of each scanning, the measurements obtained on each step are saved in a work file (generally not used), and three values are saved on the file

* if there is a peak (i.e. if the maximum intensity is not on the extreme left or right scanning step), the maximum intensity and the two adjacent intensities are saved ;

* if there is no peak, the intensity observed on the current peak position and on the two adjacent steps are saved.

The analysis of 10 elements in one sample takes around 100 seconds, including 30 seconds of depollution.

In the combined system used before, and although the monochromator could be used separately, it was generally used in combination with the polychromator, generally in the same sequence. We are know using the two independent spectrometers as follows :

Data Correction with the Scanning Monochromator

Compared with the correction procedure described for the polychromator, the procedure for monochromator is also based on the comparison with the control sample, but it is more simple. As the monochromator is not used for major element determination, there is no need for curvature correction. Due to much better resolution, there is also, in the general case, no need for interference correction. If needed, it is made in the same way as for the polychromator.

A difference with the polychromator is that, instead of a single maximum intensity, we have, for each element in each sample, three values. They can be used in three different ways, depending on the type of element:

* in the general case, only the maximum intensity is used ;

* for less emissive elements, with no clearly defined peak, it is better to use the mean value of the three data ;

* for highly emissive elements, because of the high resolution, the peak is too sharp, as compared with the width of the scanning step, to be accurately represented by the maximum intensity. In this case, the solution proposed by the Jobin-Yvon software is to fit the three data around the maximum to a Gaussian equation and to take the calculated maximum of this Gaussian as the true maximum.

body

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