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LEAD AND COPPER ABUNDANCE DETERMINATION IN PLUTONIC ROCKS BY ANODIC STRIPPING VOLTAMMETRY **

Riassunto. — È stato messo a punto un metodo per l'analisi di piombo e rame nelle rocce ignee mediante la tecnica della voltametria di rimozione anodica. Nel presente lavoro sono discusse precisione ed accuratezza del metodo.

Abstract. — A method of analysing lead and copper has been applied to plutonic rocks by means of anodic stripping voltammetry. Accuracy and precision are discussed here.

Introduction

The purpose of the present work is to implement a method of analysing lead and copper in plutonic rocks by anodic stripping voltammetry and to assess its precision and accuracy. This has been done by analysing standard rocks and comparing the measured values with those proposed by Flanagan (1969, 1973) and Abbey (1973).

Till now this technique had not been taken into consideration for the analysis of rock samples.

A previous work (Khasgiwale et al., 1972) considers the determination of Pb in minerals and rocks by a similar technique, i.e. the hanging mercury drop electrode voltammetry.

The technique discussed in this work allows to determine concentrations of up to 10^{-10}-10^{-11} moles/litre of a series of metals among which lead and copper.

Experimental

a) General principles

There are two phases in anodic stripping voltammetry analyses:

1) electrolytic plating during which the sample metallic ions (in solution) are reduced to metal on the mercury film of the mercury-graphite electrode (CMGE)

which has a negative potential in this phase. The plating kinetics tends to saturation; after 30' all the metal has pratically been reduced;

2) anodic stripping which consists of an inverse electrolysis during which metals are sequentially stripped out of the electrode and carried back into the solution. The stripping is obtained by linearly increasing the potential of the electrode on which metals has been deposited in the preceding phase. In this way, the intensity of the current circulating in the solution increases proportionally to the amount of metal reduced during the plating. The current intensity variations are recorded.

b) Apparatus

We used an ESA multiple anodic stripping analyzer model 2014. It consists of an electronic unit which controls the plating and stripping phases, an analytic unit made of four cells and a potentiometric recorder. Each cell contains 3 electrodes (see Fig. 1):

1) a counter platinum electrode;
2) a reference Ag/AgCl electrode;
3) a test mercury-graphite electrode.

c) Sample preparation

We prepared a solution of the following standard rocks: GRANITE ZGI-GM, GRANITE NIM-G, GRANODIORITE GSJ-JG1, DUNITE DTS-1, PERIDOTITE PCC-1 with a mixture of hydrofluoric and perchloric acid according to JEFFERY (1970) by using analitically pure reagents. At the same time we prepared a «blank» solution with the reagents only, in order to evaluate the Pb and Cu content in them. As shall be discussed here in below, the presence of Pb and Cu in the acids used to dissolve the rocks samples strongly affects the end results.
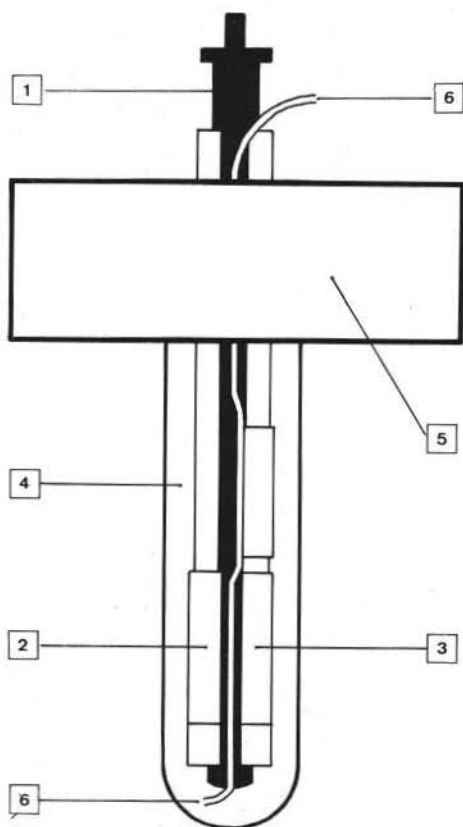

Fig. 1. — Schematic of cell holder and electrodes. 1) test electrode (CMGE); 2) counter electrode; 3) reference electrode; 4) Pyrex cell; 5) flexible cell head; 6) bubbler for nitrogen.

d) Analytical procedure

Before beginning a series of analyses it is necessary to plate electrolytically a $\sim$ 10 micron thick mercury film on the test electrode; the analytical cells are rinsed with 10 % perchloric acid.

The analysis is performed on 1 ml of the hydrofluoric-perchloric solution of the rock to which 4 ml of a mixed 1 F sodium acetate - 0.2 F sodium chloride solution are added. In a previous work BORTOLUZZI et al. (in press) had noticed that this solution introduced amounts of Pb and other metals comparable or greater than those introduced by the rock itself.

We have therefore depurated the mixed 1 F NaAc - 0.2 F NaCl solution by using a mercury pool electrolytical reagent cleaner.

The electrodes are immersed into the cell containing the sample for 30' at a plating potential of −760 mV, maintaining a 0.2 atm nitrogen flux in the cell. The stripping occurs at the following operational parameters: initial potential −760 mV, sweep rate +40 mV/sec., potential upper threshold −80 mV. The current variations caused by the metal stripping were of the order of 0.1-0.5 mA. At these conditions we were able to analyze Cu and Pb, which were recorded respectively at −210 and −560 mV (see Fig. 2).

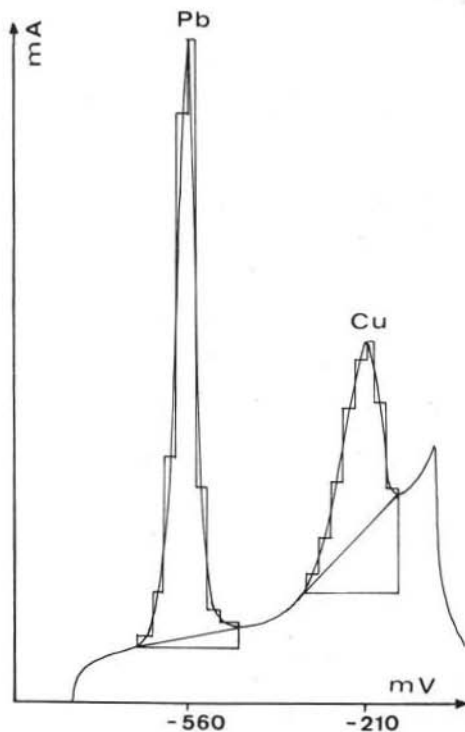On each rock sample and the « blank », five measurements of the lead and copper concentrations were performed.

Fig. 2. — Anodic stripping voltammogram of rock hydrofluoric-perchloric solution.

Each measurement consisted of:
1) four recordings of the stripping current of Pb and Cu contained in equal quantities of the hydrofluoric-perchloric rock solution, treated as described above;
2) four recordings of the same solution, to which an amount of a solution of Pb and Cu known content was added. We tried to add amounts of metals of the same order of magnitude as that presumably present in the tested solution. For both Pb and Cu the additions contained in a 10 μl volume solution were of 50 or 100 or 150 or 200 ng.

e) *Concentration computation*

We evaluated the areas under the recorded peaks by hand integrations (see fig. 2). We computed the amount of metals in the solution volume by the following formula:

$$x_s = \frac{A_s \cdot a}{A_a - A_s} \tag{1}$$

where: x_s = amount of metal in ng;
         A_s = mean of the areas under the metal peak in the sample;
         a   = amount of the addition in ng;
         A_a = mean of the areas under the metal peak in the sample with addition.

We evaluated the metal concentration in the rock by the following formula:

$$X_r \text{ (ppm)} = \frac{(x_s - x_B) \cdot V}{p \cdot v \cdot 1,000} \tag{2}$$

where: x_B = amount of metal in the « blank » contained in v;
         V = volume of the hydrofluoric-perchloric solution;
         v = solution volume;
         p = rock powder weight.

Results and discussion

TABLE 1

Analytical results of lead and copper concentration

	ROCKS	REF.	$\bar{x}$ (n)	s	C
LEAD	GRANITE	ZGI-GM	30.2 (5)	5.0	16.7
	GRANITE	NIM-G	34.2 (5)	14.5	42.2
	GRANODIORITE	GSJ-JG1	19.7 (5)	10.9	55.5
	DUNITE	DTS-1'	11.0 (5)	4.4	40.0
	PERIDOTITE	PCC-1	9.8 (5)	5.9	60.2
COPPER	GRANITE	ZGI-GM	14.9 (5)	3.9	25.8
	GRANITE	NIM-G	3.6 (5)	1.4	38.8
	GRANODIORITE	GSJ-JG1	1.3 (3)	1.2	88.6
	DUNITE	DTS-1	8.4 (5)	1.9	23.6
	PERIDOTITE	PCC-1	8.3 (4)	0.8	9.6

$\bar{x}$ (n) = arithmetic mean in ppm (n. of determinations);   s = standard deviation;

C = relative standard deviation, $\frac{s}{\bar{x}} \cdot 100$.

Table 1 shows the mean concentrations of lead and copper, the standard deviations, the relative standard deviation for every standard rock.

a) Precision

The measurements of the areas under the peaks show a good precision, having an average relative standard deviation of 10 %. Also the measurements of the metal concentrations in the solutions show a good precision, with a relative standard deviation ranging from 10 to 30 %, as can be noticed in table 2.

The measurements of the metal concentrations in the rocks show a poorer precision. We tried to evaluate whether the measurements of the metal concentrations in the rock belonged to the same statistical population. To prove this, for each rock we plotted the graph shown in fig. 3.

For each measurement these graphs show the maximum and minimum value of the metal concentration in the rock depending on the fluctuations (mean value ± 1 standard deviation) of the measurements of the areas under the peaks of the sample and of the sample plus the addition. In all cases we estimated that the measurements

TABLE 2

Comparison between the concentration measurement precisions in perchloric-hydrofluoric solution and in rock

	ROCKS	$\bar{x}_s$	s_s	c_s	c_r	$\bar{x}_B$
LEAD	GRANITE ZGI-GM	267.1	25.8	9.7	16.7	112.3
	GRANITE NIM-G	278.0	75.2	27.0	42.2	99.9
	GRANODIORITE GSJ-JG1	204.1	46.2	22.6	55.5	99.9
	DUNITE DTS-1	168.2	22.3	13.3	40.0	112.3
	PERIDOTITE PCC-1	160.9	29.3	18.2	60.2	112.3
COPPER	GRANITE ZGI-GM	82.6	19.8	23.9	25.8	6.1
	GRANITE NIM-G	65.1	7.3	11.3	38.8	46.2
	GRANODIORITE GSJ-JG1	52.8	5.8	10.9	88.6	46.2
	DUNITE DTS-1	48.6	10.1	20.7	23.6	6.1
	PERIDOTITE PCC-1	47.0	4.0	8.5	9.6	6.1

$\bar{X}_s$ = mean values of concentrations in the solution (ppb). S_s = standard deviation in the solution (ppb). C_s = relative standard deviation of concentrations in the solution (ppb). C_r = relative standard deviation of concentrations in the rock (ppm). $\bar{X}_B$ = mean values of concentrations in «Blank» (ppb).

belong to the same population. The relative standard deviations of the Pb concentrations in the rock range between 15 and 60 %. 60 % of the measurements belong to the range $\bar{x} \pm s$, the remaining 40 % to the range $\bar{x} \pm 2s$. The relative standard deviations of the Cu concentrations in the rock range between 10 and 90 %; 72 % of the measurements fall into the range $\bar{x} \pm s$, the remaining 28 % in to the range $\bar{x} \pm 2s$. The relative standard deviation values we obtained fully agree with those reported by BROOKS et al. (1978) for measurements of trace element concentrations in G1 and W1 standard rocks. The relative standard deviation computed by using the data reported by FLANAGAN (1976) for the PCC-1 peridotite

and for the DTS-1 dunite (PCC-1: 41.6 for Cu, 42.5 for Pb; DTS-1: 57.3 for Cu, 46.6 for Pb) is similar to that we obtained on the same samples (see table 1).

The method is more precise for the measurements of metal concentration in hydrofluoric-perchloric solution than for the measurements of the metal concentration in the rock; this can be explained by looking at equation (2) in which the metal concentration value in the rocks also depends on the metal concentration value x_B in the « blank ».

In table 2 one can actually notice that in those samples where the difference $x_s — x_B$ is small, the relative standard deviation values of the metal concentration in the rock are high.
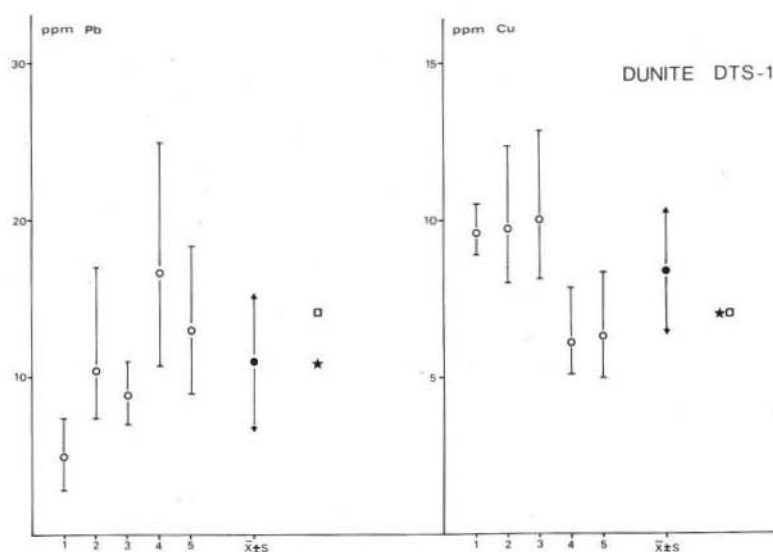

Fig. 3. — Statistical comparison between concentration measurements and standard rocks (□ Flanagan value, ★ Abbey value).

b) *Accuracy*

JEFFERY (1970) proposed to compute the accuracy by subtracting the « true value » from the measurement mean; the same author affirms that the accuracy is difficult to evaluate because the « true value » changes with the implementation of more and more precise methods of analysis.

As it can be noticed in table 3, FLANAGAN (1973) and ABBEY (1973) give different values for the same elements as results of analyses in the same rocks.

FLANAGAN (1973) classifies the concentration values as « recomended, averages, magnitudes »; ABBEY (1973) calls « usable » his proposed data, and puts a question mark near the less reliable ones.

Table 3 shows the accuracy values, computed according to the data proposed by FLANAGAN (1973) and according to the values proposed by ABBEY (1973). It can

be noticed that the standard rock values FLANAGAN (1973) proposes for Pb are all in the range $\bar{x} \pm s$; while, as far as Cu is concerned, the values referring to NIM-G granite and to PCC-1 peridotite do not come into that range. The accuracy of the Pb concentration values is therefore higher than the accuracy of the Cu concentration values.

By making use of the « true value » proposed by ABBEY (1973), the concentration measurements become more accurate, especially the lead ones.

TABLE 3

Comparison between measured means and literature data

ROCKS	$\bar{x}$	s	$\bar{x}$ Flanagan	$\bar{x}$ Abbey	Acc.Fl.	Acc.Ab.
LEAD						
GRANITE ZGI-GM	30.2	5.0	30 (rec.)	30	+0.2	+0.2
GRANITE NIM-G	34.2	14.5	38 (aver.)	35?	-3.8	-0.8
GRANODIORITE GSJ-JG1	19.7	10.9	24 "	24?	-4.3	-4.3
DUNITE DTS-1	11.0	4.4	14.2 "	11	-3.2	0.0
PERIDOTITE PCC-1	9.8	5.9	13.3 "	10	-3.5	-0.2
COPPER						
GRANITE ZGI-GM	14.9	3.9	13 (rec.)	13	+1.9	+1.9
GRANITE NIM-G	3.6	1.4	15 (aver.)	13	-11.4	-9.4
GRANODIORITE GSJ-JG1	1.3	1.2	3.3(magn.)	7?	-2.0	-5.7
DUNITE DTS-1	8.4	1.9	7 (aver.)	7	+1.4	+1.4
PERIDOTITE PCC-1	8.3	0.8	11.3 "	11	-3.0	-2.7

Conclusions

From the obtained results we can draw the conclusion that the anodic stripping voltammetry method is quite valuable for determining Pb and Cu concentrations in plutonic rocks.

In particular, the results relating to Pb concentrations are characterized by a higher accuracy and lower precision and those relating to Cu concentrations by a lower accuracy and a higher precision.

Furthermore the precision and detection threshold of the method depend upon the purity of the hydrofluoric and perchloric acids, which, even when of analytic quality, are not sufficiently pure for this type of analysis.

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