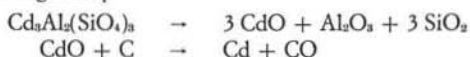


AMBROGIO MAZZUCOTELLI *, MARCO BOY *, RICCARDO VANNUCCI **

SOLID SAMPLING AND FLAMELESS ATOMIC
ABSORPTION DETERMINATION OF CADMIUM TRACE
AMOUNT IN ROCKS AND MINERALS

ABSTRACT. — A flameless atomic absorption determination of cadmium in rocks and minerals is described. The electrothermal atomization was performed on a solid sample to avoid long manipulations to solubilize rock samples. Such procedures are considered as source of errors owing to the volatilization of elements such as cadmium, mercury, lead, thallium etc. A standard addition method is described and cadmium values of NIMROC international standards are given. A good application to geochemical prospecting is expected.

RIASSUNTO. — Nel presente lavoro viene descritto un metodo per la determinazione di quantità in tracce di cadmio nelle rocce e nei minerali: la tecnica impiegata è la spettrometria di assorbimento atomico senza fiamma con campionamento solido della sostanza da analizzare. In natura il cadmio oltre che nei suoi minerali, monteponite (CdO), otavite (CdCO₃), hawleyite e greenockite (CdS nelle forme alfa e beta), è presente anche nei minerali di zinco. Alcuni autori inoltre hanno studiato silicati di cadmio con struttura simile ai granati. Di particolare importanza è la forma sotto la quale sono presenti le eventuali tracce di cadmio: consente infatti di spiegare le possibili reazioni di decomposizione e riduzione con il carbone della grafite che si verificano durante l'atomizzazione del campione ad elevate temperature. Un generico schema di reazione proposto è il seguente:



Il silicato complesso, ad una temperatura sufficientemente elevata si decompone in una miscela di ossidi: questi a contatto con il carbone liberano gli atomi di metallo che subiscono l'assorbimento atomico. Vengono inoltre studiate le interferenze dovute a composti volatilizzati sotto forma molecolare. Il programma a gradiente elettrotermico illustrato permette una separazione fra i picchi dovuti all'atomizzazione del cadmio e quelli dovuti alle interferenze. Tale separazione consente di evitare il controllo del fondo spettrale con la lampada a deuterio. Le analisi vengono condotte a due diverse lunghezze d'onda: 228,8 nm per le quantità inferiori a 5 ppm e 326,1 nm per quelle superiori a tale valore.

Per l'analisi viene usato il metodo delle addizioni standard: allo scopo si effettuano delle aggiunte di 2 e 4 microlitri di una soluzione standard di cadmio in modo da avere delle quantità assolute dell'ordine di 10⁻¹³ grammi di metallo. Tali aliquote vengono introdotte in apposite microcoppe di grafite, che riscaldate su piastra anch'essa di grafite, evaporano le soluzioni addizionate.

Successivamente vengono pesati pochi milligrammi di campione, finemente polverizzato. I valori ottenuti dopo aver sottoposto ad atomizzazione le tre coppe con il loro contenuto vengono interpolati con il metodo della regressione lineare. Per la valutazione dei picchi è stata presa in considerazione l'area calcolata mediante un integratore elettronico. I valori ottenuti su 6 campioni di rocce internazionali (NIMROC del South African Bureau of Standards) si sono rivelati in ottimo accordo con i ranges pubblicati in letteratura.

* Istituto di Petrografia dell'Università di Genova. ** Istituto di Geologia dell'Università di Urbino.

Introduction

Atomic absorption spectrophotometry (AAS) based on atomization in flames is now the most popular analytical method with rock analysts for simple, rapid and inexpensive determination of a large number of major, minor and trace elements in geological materials.

During recent years much work has been devoted to the problem of replacing the conventional method of atomization in flames by more sensitive methods. Among the new techniques atomization in flameless systems has been found particularly promising.

Pioneer work on the construction, theory and application of electrothermal atomization cells for analytical purposes was started by L'Vov in 1959. Compared with flame atomization, the non-flame cells have the advantages of requiring smaller amounts of sample, having lower limits of determination and being well suited for direct atomization of minor and trace elements from solid samples.

The principle of analysing geological materials by atomizing the components directly from the solid state offers some definite advantages: the time-consuming decomposition step can be omitted, and the analysis can be carried out without addition of reagents and without any separation and concentration steps: the risks of introducing contamination and of losing the element to be determined are thus considerably reduced. The disadvantages of direct AAS analysis of solid geological materials are that the method is destructive, normally only one element can be determined at a time and the use of small samples may introduce serious sampling errors. The analyses directly performed on solid geological samples take into account only the elements with a low temperature of atomization, i.e. lead, thallium, mercury, cadmium, bismuth, zinc and sometimes silver. EMMERMANN and LUECKE (1969) presented a new analytical method for geochemical prospection based on soil samples from the environment of lead-zinc-silver-containing rocks. This method was a modification of the normal AAS using a heat-resisting evaporation boat made of tantalum metal. The detection limits were: Pb = 2 ppb, Zn = 0.05 ppb and Ag = 0.2 ppb.

Flameless atomic absorption spectrophotometric methods for the microanalysis and trace element analysis of rocks are described by HEINRICHS and LANGE (1973). The microanalysis of the elements Al, Fe, Mn and Ti so far determined can be carried out in the diluted solution of the digested samples without additional separation.

In the case of trace element analysis the elements may be determined either directly in the solution (Sr, Pb) or after separation.

Separation can be carried out by extraction from the solution (Tl) or by the volatilization technique with the solid substance heated to 1000-1200° C (Tl, Pb, Cd, Bi). For mercury the method of electrolytical separation together with the volatilization technique is considered suitable.

Two methods for rapid determination of thallium and cadmium in silicate materials by flameless AAS after extraction of thallium as bromide into isopropylether and of cadmium with amines, after decomposition with HF-HClO₄ are described by SIGHINOLFI (1973) and SIGHINOLFI and SANTOS (1976).

Atomic absorption spectrometric determinations of silver, bismuth and cadmium in the Canadian SU-1 and Nordic ASK reference sulfide ores, and in a series of Norwegian sulfide ores of technical importance, were carried out by atomising the elements directly from the solid state. Atomizations were made in a high-frequency induction-heated graphite furnace. For comparison purposes, samples were also decomposed, and analyses made by atomizing sample solutions in the furnace and in the flame (LANGMYHR et al., 1973).

GOVINDARAJU et al. (1974) have developed a singular non-solution flame atomic absorption procedure for the determination of trace levels of lead down to 1 ppm in silicate rock samples. Powdered rock sample is impregnated uniformly on an iron screw rod which is then burnt in the air-acetylene flame of an atomic absorption spectrometer. The recorded absorption curve (peak area) is proportional to the lead content of the sample.

LANGMYHR et al. (1974) described AAS methods for the determination of cadmium, lead, silver, thallium and zinc in some international and other silicate rocks. The metals are atomized directly from the solid samples in a graphite furnace. The data are compared with results obtained by atomising solutions in the flame, in the graphite furnace and with earlier data.

Finally GONG and SUHR (1976) described the use of graphite-furnace AAS for the determination of cadmium in rocks and sediments by direct atomization from the solid state. At the 10-1000 ppb level, the relative standard deviation was 10-20 %. Samples were ground to 100 mesh and, if necessary, 325 mesh before analysis. Two resonance lines were employed: 228.8 nm for less than 5 ppm cadmium and 326.1 nm for levels above 5 ppm. Results are given for a series of standard rocks and for stream sediment samples.

In order to improve the applicability of solid sampling we have studied the atomic absorption of cadmium using a standard addition method directly performed on the powdered sample. Few microliters of cadmium solution were added and dried to the weighed portions of international silicate rock samples. As cited above (GONG and SUHR, 1976) we have employed two wavelength related to the cadmium contents of the analysed rocks. A gradient-temperature program for the atomization of the sample was used.

Reactions involved in flameless AAS procedures

In nature cadmium is exclusively known as occurring in compounds. In some cases it replaces other elements in their minerals, especially zinc. The most common cadmium minerals are: monteponite (CdO), otavite (CdCO₃), hawleyite and greenockite (CdS in its alpha and beta form) (BREHELER, 1972).

During weathering, cadmium goes into solution containing sulfate and chloride. Under conditions of strong oxidation cadmium forms oxidized minerals, such as CdO and CdCO₃. Cadmium has a strong affinity for sulphur and is a typical chalcophile element (GOLDSCHMIDT, 1958). This explains its preferred accumulation in magmatic sulphides (IVANOV, 1961). Owing to its weaker oxyphile character, cadmium becomes nearly quantitatively enriched in hydrothermal rocks and minerals (RANKAMA and SAHAMA, 1961).

The highest concentration of cadmium is found in sphalerite. Cadmium is also present in galena, boulangerite and boumonite. In oxidized zones cadmium is found in smithsonite, sauconite, manganese oxides and limonite (WAKITA, 1970).

However cadmium has been found as substitute in silicates such as garnets (GENTILE and ROY, 1960; MILL, 1964) and in other silicate structures (DENT GLASSER and GLASSER, 1964; DENT GLASSER, 1965).

The knowledge about the crystal-chemical forms of cadmium is useful to try to explain the possible reactions with carbon of graphite furnace at the high temperatures which occur during the atomization stage. The reactions of geological materials during heating in atomization cells are complicated by the non-equilibrium conditions which may prevail during many atomization processes.

However, some of the reactions that have been studied and some that are likely to occur when geological materials are heated in carbon atomization cells and in an inert atmosphere will be discussed shortly (LANGMYHR, 1977). During the drying at about 100° C the main reaction is the removal of hygroscopic water. However, some volatile elements, such as mercury, may be lost during this operation. The main purpose of the ashing step is to destroy organic matter: that isn't the case of many geological samples. When the samples contain hydroxides, carbonates, sulphates, nitrates etc., it is recommended that before atomization the salts should be converted into the corresponding oxides by heating at 800-1000° C. Atomizations are made at temperature ranging from below 1000° C up to about 3000° C. On heating, most silicate minerals and rocks behave like weakly associated aggregates of simpler oxide groups; at temperatures above 1000° C, the silicate lattices break down and a melt is obtained. In general terms, molecular dissociation occurs in several steps depending on the anionic composition of the original matrix. Oxy-anion salts, such as phosphates, sulphates or nitrates, often give better results than halide salts, since many halide salts may vaporize directly as molecules at higher temperatures whereas most oxy-anion salts first decompose to their corresponding metal oxide. The metal oxide is then thermochemically reduced to free atoms. Once the salt has decomposed, the atomization behaviour depends on the thermal stability and volatility of the metal oxides (CULVER, 1975). Several atomization mechanisms have been proposed (FULLER, 1972, 1974; OTTAWAY and CAMPBELL, 1974; AGGET and SPROTT, 1974).

CAMPBELL and OTTAWAY (1974) postulated the reduction of the metal oxide by the hot graphite in the following way:



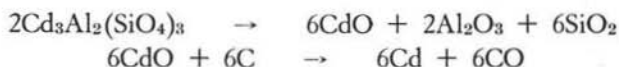
Using this model for the atomization mechanism and assuming that the graphite reduction is rapid, they compare the temperature of the first appearance of atomic vapour to the calculated temperature at which the free energy for the reaction became negative.

However, they used a Massmann type furnace which has a much higher thermal inertia than the carbon rod atomizer and as a result, heats relatively slowly. FULLER (1974) pointed out for these atomizers the rate-controlling step in the production of atoms is probably the carbon reduction step. However, if high temperatures are reached quickly, as in the case with the carbon rod atomizers, kinetic factors associated with the graphite reduction step of the molecular dissociation are minimized and the production of atoms is governed more by the thermodynamic stability of the metal oxide. Dissociation of the metal oxide occurs at constant ambient pressure and depends on the partial pressure of the oxygen radical. At thermodynamic equilibrium the above cited dissociation reaction is subject to the law of mass action and is governed by the reaction:



MAESSEN and POSMA (1974) stated that the concentration of CO molecules is controlled by the amount of oxygen absorbed on the graphite, the amount of oxygen liberated during atomization, and the oxygen content in the inert gas. AGGETT and SPROTT (1974) found that many atoms vaporize at temperatures below their boiling points, while others require atomization temperatures in excess of their boiling points. Comparing the vapor pressure at the temperature where atomization became evident and the values for the free energy for the dissociation of the metal oxides, they concluded that the vapor pressure of the element and the thermal stability of the metal oxide as well as the reducing properties of the graphite influence atomization behaviour.

Related to the cadmium behaviour, these considerations can be digested as follows: in the most general case cadmium may be considered (especially when present at trace amounts) as substitute in a silicate lattice; at a sufficiently high temperature the silicate lattice break down and an oxides melt is obtained (LANGMYHR, 1977); when the atomization is performed above 800° C the cadmium oxide decomposes with subsequent production of free metal atoms. Chemical reaction, considering an atomization at about 1100° C, may be considered as follows:



In the case of the other cadmium minerals such as oxide, sulphate carbonates and nitrates the decomposition step (pyrolysis) is clear. When sulphide minerals and ores are heated they give off sulphur (LANGMYHR, 1977).

Interferences

In flameless AAS, the major interference occurs when some of the light is absorbed or scattered by molecules or solid particles (non-atomic species) in the light path. These interferences are usually called «background» absorption. Generally the causes of background absorption are identified as molecular absorption or light scattering. Light scattering can occur when solid particles cross the light path and it is evident as smoke particles. Molecular absorption arises when salts are vaporized as complete molecules. If the molecules are generated in the light path at the same time as the atoms of interest, the resulting absorption signal will be the sum of the two components (CULVER, 1975). This problem occurs particularly where samples of high salt content are analyzed for elements whose wavelength is below about 350 nm. Appropriate choice of the ash conditions can often remove the problem by removing these molecules before atomisation, but this may not be completely possible where the element of interest has a low boiling point.

The halide molecular absorption curves (CULVER, 1975) show that these compound interfere particularly in the range containing the resonance lines used for cadmium determinations.

Nevertheless the halides content of the common silicate rocks may be supposed as particularly low.

GONG and SUHR (1975) recorded an absorption peak, appearing just after the atomization peak of cadmium, which was supposed due to «interference from furnace». But in their work it is not completely clear if such a peak disappears with deuterium background correction because the comparison has been made at two different wavelengths (228.8 and 326.1 nm). In our tests we also noted such an interference peak which disappears by using a deuterium arc corrector.

We want to stress that when short atomization times (STEP MODE) are used the overlapping of this peak with the cadmium atomization peak is too high to allow to a good analytical evaluation.

At this purpose we use a RAMP MODE of atomization (50° C/sec. to a maximum temp. of 1300° C) which has allowed to the complete separation of the two peaks.

Tests performed with cadmium and sodium chloride, showed that the interference peak due to NaCl molecular band has a behaviour which is very much alike to the above cited interference.

Moreover these experiments carried out on synthetic solutions showed that sodium has an antiionization power on the absorption peak.

As cited by GOVINDARAJU et al. (1974) the same amount of volatile elements (in this case cadmium) in different matrices don't give comparable heights of the peaks: in this case the peak area is more expressive.

Procedure

A Jarrel-Ash « Atomsorb » Spectrophotometer equipped with a Varian-Techtron Carbon-Rod Atomizer (mod. CRA-63) was used. Graphite cups were used for the measurement and a graphite plate was used for the routine drying.

The atomization program is as follow:

DRY STAGE	80° C for 15 seconds
ASH »	200° C for 30 seconds
ATOM. »	50° C/sec. to a max. temp. 1300° C
(RAMP MODE)	

The conversion from voltage to temperature setting was made by the calibration graphs published by CULVER (1975).

An high sensitivity (± 0.000001 mg) balance (Mettler) was used. Oxford and Eppendorf micropipettes were used for microsampling.

An electronic integrator, INFOTRONICS, and microcomputer Hewlett and Packard HP-25 were used to integrate peaks and to compute results.

Pipette 2 and 4 microliters of a 0.025 ppm cadmium standard solution (to have two corresponding amounts of $5 \cdot 10^{-13}$ and $1 \cdot 10^{-12}$ grams of Cd) in two different graphite cups. Place these cups on an apposite graphite plate and dry to complete evaporation of the water. Cold and weigh the two cups and another one.

Weigh out three aliquot of finely powdered rock sample of about 3 mg (± 0.000001) in the above cited graphite cups. Select the desired wavelength 228.8 for amounts at below of 5 ppm and 326.1 for above 5 ppm of cadmium. Insert each cup between the electrodes and start the atomization program. As discussed above the electrothermal gradient of the atomization program reaches possible the separation of the atomization peak from the interference peak without correction of background with deuterium lamp; for this reason the values to be considered are the first of the sequence of the peaks. The peak areas are plotted in the linear regression program of the Application Program Library of Hewlett-Packard.

Results and discussion

The analyses were carried out on six samples of international standard rocks supplied from the South African Bureau of Standards. Results are listed in table 1.

The sensitivity (absorption related to 1% of the scale) was calculated in $1 \cdot 10^{-14}$ grams of cadmium while the detection limit is the half about. As showed above the result obtained are in agreement with the literature values. However we retain that the proposed method can be considered as an improvement of existing techniques as showed by the following points:

a) the atomization program using an electrothermal gradient makes possible to

avoid the use of a background corrector what (when a singlebeam instrument is used) represents a very time-consuming step!

- b) some authors (LANGMYHR et al., 1974 and GONG and SUHR, 1975) used the standard addition method for a solubilized sample which is then used as reference sample for all the calculations. The mixed solid-liquid standard addition method proposed makes possible a single calculation for each powdered sample.

TABLE 1
Cd contents of NIMROC reference samples

	Cd ppm	Ref. value*
NIM G granite	4.2	1 ± 5
NIM S syenite	15.4	1 ± 35
NIM L lujavrite	2.6	2 ± 4
NIM N norite	2.2	1 ± 4
NIM P pyroxenite	1.8	0.5 ± 3
NIM D dunite	2.0	4

* STEELE et al., 1978.

Finally, in spite of the precision of good results obtained, we retain that the best application of the proposed method can be the application to geochemical prospecting.

A more simplified procedure (determination of a reference sample only by the proposed standard addition method) reaches possible to evaluate with quickness a wide number of samples.

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