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Precipitation

NOTA: A redação, ortografia, conceitos e revisão final são de responsabilidade dos autores.

APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE DETERMINATION OF MINOR AND TRACE ELEMENTS IN MAGNESITE ORES *

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ABSTRACT

A method employing analysis with thermal neutrons was developed for analyzing magnesite samples coming from the States of Ceará and Bahia (Brasil). Ten samples were analyzed.

Qualitative analysis of the samples indicated the presence of Mn, Fe, Sc, Ca, Cu, Co and some of the lanthanides.

Mn was analyzed by non-destructive activation analysis and the other elements were analyzed, individually or in group, after sample dissolution with 8 N HCl solution.

A detailed study of the possible interferences in neutron activation analysis of the elements considered was also undertaken. The precision and accuracy of the results obtained and the sensitivity of the method are discussed.

INTRODUCTION

The recent progress in the geochemistry field is closely linked with the interpretation of the relationships found among the concentrations of elements present in minerals of different deposits.

According to Morrison[15], based in the geochemical classification of the elements by Goldschmidt[9], "every element is of potential geochemical interest, since with the knowledge of elements abundances in various samples, the geochemist can formulate hypotheses and test theories for the formation, distribution and chemical and physical interactions of the various minerals that have finalized a particular rock, soil or ore composition".

Therefore, advancement in geochemistry needs chemical methods of analysis having great precision, accuracy and sensitivity. Since neutron activation analysis fulfills the requirements to be applied for analyzing the majority of the elements, this technique has, very often, been used for analyses of materials from the geochemical standpoint.

This paper presents the application of neutron activation analysis to magnesite ores. Magnesite deposits from the states of Ceará and Bahia had already interested Bodenlos[3,4], from the geochemical point of view. However, some minor and trace elements were not hitherto analised in these ores.

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The first step of the present work was to carry out the qualitative analysis of the samples. After pulverization, homogenization and irradiation of samples under a thermal neutron flux, the gamma-rays spectrum showed the characteristic lines of ^{56}Mn, ^{59}Fe, ^{46}Sc, ^{47}Sc, ^{64}Cu, ^{60}Co and of some radioisotopes of the lanthanide elements.

Only manganese was determined by instrumental activation analysis, since all other elements needed chemical separation after sample's irradiation, in order to get a better sensitivity in their determination.

The procedure applied to the chemical separations is simple, in as much as it is not necessary to change the medium throughout the whole analytical procedure. Iron was separated by solvent extraction because of the good results previously achieved in extractions carried out with ethyl ether and isopropyl ether from HCl solutions[1,2,8,19]. Since magnesite samples were dissolved with HCl, the solvent extraction technique was the most suitable for iron separation. The determination of scandium and calcium (through the activities of ^{46}Sc and ^{47}Sc) was performed after the separation of scandium by partition chromatography. Qureshi et al.[17] showed that retention of scandium by di(2-ethylhexyl) phosphoric acid (HDEHP) absorbed in kieselguhr, it almost complete and is not dependent on HCl concentration. The ratio between the mass of HDEHP and that of kieselguhr used in this work was the same used by Samsahl[18] for scandium separations. It was possible to achieve the simultaneous analysis of scandium and calcium by measuring the activities of ^{46}Sc and ^{47}Sc formed in the following nuclear reactions:

$$^{45}Sc\ (n,\gamma)\ ^{46}Sc$$

$$^{46}Ca\ (n,\gamma)\ ^{47}Ca \xrightarrow{\beta^-} {}^{47}Sc$$

since the gamma-rays emitted by these radioisotopes have quite different energies. The separation of copper and cobalt from the lanthanides was carried out by ion exchange, since copper and cobalt form the complexes $(CuCl_3)^-$ and $(CoCl_3)^-$ in HCl solutions. The behaviour of these complexes has already been extensively studied and it was shown[10-14] that retention of $(CuCl_3)^-$ and $(CoCl_3)^-$ by the exchanger starts from HCl solutions whose concentrations are 4.5M and 2.5M, respectively. Since the lanthanides do not show the same behaviour as copper and cobalt, whatever may the HCl concentration be, they pass through the ion exchanger column and may be quantitatively precipitated as oxalates in the effluent solution from the resin, after elimination of HCl excess.

Thus, a very simple radiochemical separation procedure was established, in which the elements to be analysed may be grouped into only four groups, namely:

1) Iron – Separated by solvent extraction.

2) Scandium (and calcium) – By using partition chromatography.

3) Copper and cobalt – Ion exchange separation.

4) Lanthanides – Precipitation as oxalates.

INTERFERENCES

Some interferences which may occur in activation analysis depend on the intensity of the neutron flux as well as on the ratio between thermal and epithermal neutron fluxes. In this work, the

magnesite samples were irradiated in a thermal neutron flux of about 5×10^{12} n cm^{-2} sec^{-1} and the ratio between the thermal and epithermal neutron fluxes was of nearly 100.

The following interferences may occur when the elements mentioned in the introduction of this paper are determined by activation analysis:

a) In Manganese Determination

The presence of iron and cobalt may impair the accuracy of analytical results for manganese, because of the following nuclear reactions:

$$^{56}Fe\ (n, p)\ ^{56}Mn\ (\sigma = 0{,}44\ mb)$$

$$^{59}Co\ (n, \alpha)\ ^{56}Mn\ (\sigma = 35\ mb)$$

$$^{54}Fe\ (n, \gamma)\ ^{55}Fe \xrightarrow{EC} {}^{55}Mn\ (n, \gamma)\ ^{56}Mn$$

The activity of ^{56}Mn, from the first and second reactions, will depend on iron and cobalt concentration present in the samples. Since in the magnesite ore samples dealt with in this work the concentration of cobalt is very low and iron concentration is of about 1% or less, the contribution of the activity of ^{56}Mn coming from these reactions is negligible. Moreover, irradiations were always carried out in a well thermalized neutron flux.

As far as the second order reaction is concerned, Op de Beeck[16] estimated that, when irradiated with a thermal flux of 5×10^{12} n cm^{-2} sec^{-1} for 8.25 hours, pure iron gives rise to an activity of ^{56}Mn as if 1.74×10^{-6} ppm of manganese were present. The irradiation conditions used in this work were, approximately, the same as those applied by Op de Beeck[16] in his investigation, therefore, the contribution of the second order reaction for the ^{56}Mn activity was also negligible.

b) In Iron Determination

The nuclear reaction:

$$^{59}Co\ (n, p)\ ^{59}Fe\ (\sigma = 22\ mb)$$

shows that cobalt may be an important interference when its concentration, in samples irradiated in a not well thermalized neutron flux, is high. Taking these conditions into account, the interference brought by cobalt may be neglected, mainly considering the very low concentration of this element in the samples.

c) In Scandium Determination

Calcium may interfere through the following reaction:

$$^{44}Ca\ (n,\gamma)\ ^{45}Ca \xrightarrow{\beta^-} {}^{45}Sc\ (n,\gamma)\ ^{46}Sc$$

As stated by Op de Beeck[16], the amount of ^{46}Sc produced by the irradiation of 1 g of pure calcium is the same as that coming from irradiation of about 0.5 μg of scandium, if irradiation conditions are the ones used in this work.

Since calcium concentration in the analysed samples is less than 1%, the interference of this reaction may be considered meaningles.

d) In Cobalt Determination

Copper as well as iron may interfere in cobalt determination by activation analysis, considering the nuclear reactions:

$$^{63}Cu\ (n,\alpha)\ ^{60}Co \quad (\sigma = 0.36\ mb)$$

$$^{58}Fe\ (n,\gamma)\ ^{59}Fe \xrightarrow{\beta^-} {}^{59}Co\ (n,\gamma)\ ^{60}Co$$

The first reaction is negligible because of the cross-section value, the amount of copper in the samples and the well thermalized neutron flux used for samples irradiations.

According to Op de Beeck[16], the second order nuclear reaction is also negligible, since, by this reaction, pure iron gives rise to about only 5.2×10^{-7} ppm of cobalt, if the calculation is made taking into account the ^{60}Co activity formed, when the irradiation conditions are the same as those already described.

EXPERIMENTAL

Preparation of Samples

The samples analysed in this work were supplied by "Magnesita S. A." and "Magnesium do Brasil" industries.

In order to simplify the identification, the samples were labelled according to type and origin, as shown in Table I.

Table I

Type and Origin of Magnesite Samples

Label	Type	Origin
I	Castela	Serra das Éguas – Brumado – (Bahia)
II	Pedra Preta	Serra das Éguas – Brumado – (Bahia)
III	(*)	Pirajá – Brumado – (Bahia)
IV	Branca	Serra das Éguas – Brumado – (Bahia)
V	Pedra Preta	Brumado – (Bahia)
VI	(*)	Alencar – Iguatú – (Ceará)
VII	Pedra Preta	Iguatú – (Ceará)
VIII	(*)	Pitombeiras – Iguetú – (Ceará)
IX	(*)	Torto – Jucas – (Ceará)
X	(*)	Riacho Fundo – Jucas – (Ceará)

(*) No specification

The samples were broken into pieces of about 3-5 mm by means of a hammer covered with a polyethylene sheet in order to avoid contamination. Then, the samples were quartered, grinded in an agate mortar and involved with aluminum foil for irradiation.

Apparatus

The counting equipments used for gamma-ray spectrometry were:

1) TMC Model 406-2, 400-Channel analyzer coupled to a well-type 7.5 x 7.5 cm NaI(Tl) detector.

2) Nuclear Chicago 4096-Channel analyzer coupled to a coaxial 27.8 cm^3 Ge-Li detector, Model 8001-0424. The energy resolution of the system is 3.8 keV (fwhm) for the 1332 keV ^{60}Co line.

Reagents

Besides the usual chemical reagents, all of them of analytical grade, the following were also used:

Silanized Kieselguhr – 0.2 to 0.3 mm – Merck

Anionic Resin Amberlite CG-400 type I – 100-200 mesh

Isopropyl ether p.a.

Deionized water was used in all the experiments.

Preparation of Carrier and Standard Solutions

Carrier solutions were prepared by dissolution of the elements or their oxides with suitable reagents. The solutions were diluted with water until the concentration of the element was of about 10 mg/ml.

Standard solutions were prepared as the preceding ones, but their final concentration was in the range of 40 μg/ml to 20.0 mg/ml, according to the good or poor nuclear characteristics for activation analysis of the isotopes taken into account.

Irradiation standards were prepared by drying 25μl of the suitable standard solution over about 1 cm^2 of Whatman nº 40 filter paper. Radioactive tracer solutions were also prepared in order to determine the chemical separations yields.

Procedure

a) Non-Destructive Activation Analysis

About 100 mg of ore sample and a manganese standard were activated for 30 minutes. After the decay of ^{27}Mg activity, the gamma-ray spectrum was recorded by means of a NaI(Tl) detector and the quantitative analysis was carried out by using the area of the 846 keV photopeak of ^{56}Mn.

b) Activation Analysis with Chemical Separation

After irradiation for a period of 8 hours of 100-200 mg of magnesite sample and a standard of each element that was to be analysed, the sample was dissolved with hot concentrated HCl and 10 mg of each suitable carrier were added. The solution was dried, the residue was taken with 8 M HCl solution and the insolubilized SiO_2 was filtered off. It was verified that the activity adsorbed by the filter paper was negligible.

Iron was extracted from the sample solution (about 20 ml) with 3 x 10 ml portions of isopropyl ether.

The back-extraction of iron from the combined organic phases was accomplished by means of water (3 x 10 ml). From this solution, iron was precipitated as hydroxide by means of NH_4OH. The gamma-ray spectrum of the precipitate was recorded by using a NaI(Tl) detector. The iron concentration of the samples was calculated through the area of the 1099 keV photopeak of ^{59}Fe.

The aqueous phase remaining after iron extraction was percolated, at a flow-rate of 0.5 ml/min, through a column (diameter = 9 mm; height = 35 mm) filled with kieselguhr containing 10% HDEHP absorbed in it.

The column was washed with 8M HCl solution and the kieselguhr was removed from the column and place in a suitable counting vial.

Scandium and calcium were analyzed, respectively, through the areas of the 889 keV and 160 keV photopeaks of the gamma-rays spectra obtained by means of the NaI(Tl) detector.

The effluent from the separation of scandium and calcium was percolated through anionic resin in the chloride form at a flow-rate of 0.5 ml/min. The dimensions of the column were: diameter = 10 mm and height = 70 mm. Copper and cobalt, adsorbed by the exchanger as the complexes $(CuCl_3)^-$ and $(CoCl_3)^-$, were eluted with water. Thiourea and NaOH were added to the effluent solution from the column.

The gamma-ray spectrum of the sulphides precipitate was recorded by means of a NaI(Tl) scintillation detector. Copper was determined through the area of the 511 keV photopeak of ^{64}Cu and cobalt through the total area of the 1173 keV and 1332 keV photopeaks of ^{60}Co. Generally, cobalt analysis was made after the ^{64}Cu decay, since the ^{64}Cu 1395 keV photopeak interferes with cobalt determinations when a detector with poor resolution is used. When it was possible, the spectrum subtraction technique was used. The effluent solution from the anion exchanger was dried and the residue was taken with 0.1 M HCl solution. The elements of the lanthanide group were precipitated by adding oxalic acid solution and the gamma-ray spectrum of the insoluble oxalates was recorded by using a Ge-Li detector. Analyses of samarium, europium, cerium and lanthanum, through the characteristic lines of ^{153}Sm (103 keV), $^{152+154}Eu$ (122 keV), ^{144}Ce (145 keV) and ^{140}La (1596 keV) were possible.

Determination of Chemical Separation Yields

The behaviour of the chemical separation procedure was examinated by using a 100 mg inactive ore sample and radioactive tracers of the analysed elements. $^{152+154}Eu$ was used as tracer for the elements of the lanthanide group. The chemical separation yields were calculated by comparing the added and recovered activities. The area of the photopeaks were calculated by means of the technique indicated by Covell[6]. The results for the chemical separations yields are shown in Table II.

Table II

Chemical Separations Yields

Element	Mean and Standard-Deviation(*) (%)
Fe	93.07 ± 0.67
Sc	97.25 ± 0.44
Cu	94.23 ± 0.62
Co	94.05 ± 0.60
Lanthanides	99.87 ± 0.40

(*) Values for six determinations.

RESULTS

The results for non-destructive analyses of Mn are shown in Table III, where the means and the standard-deviations for ten determinations for each sample are presented.

Table III

Results for Mn Analyses

Sample	Mn(*) (%)
I	0.220 ± 0.004
II	0.310 ± 0.015
III	0.021 ± 0.001
IV	0.025 ± 0.001
V	0.270 ± 0.015
VI	0.035 ± 0.001
VII	0.310 ± 0.005
VIII	0.040 ± 0.001
IX	0.040 ± 0.001
X	0.042 ± 0.001

(*) Means and standard-deviations for ten determinations.

The results obtained after the chemical separation procedure, corrected by applying the chemical yields values presented in Table II, are shown in Tables IV to VII.

Table IV

Results for Fe Analyses

Sample	Fe(*) (%)
I	1.20 ± 0.08
II	0.53 ± 0.02
III	0.24 ± 0.01
IV	0.26 ± 0.01
V	0.51 ± 0.03
VI	0.57 ± 0.05
VII	0.25 ± 0.01
VIII	0.63 ± 0.01
IX	0.76 ± 0.01
X	0.74 ± 0.01

(*) Means and standard-deviations for five determinations.

Table V

Results for Sc and Ca Analyses

Sample	Sc(*) (ppb)	Ca(*) (%)
I	70 ± 3	0.65 ± 0.03
II	110 ± 8	0.13 ± 0.02
III	47 ± 7	0.090 ± 0.005
IV	24 ± 4	0.16 ± 0.01
V	110 ± 7	0.090 ± 0.008
VI	110 ± 5	0.15 ± 0.01
VII	49 ± 3	0.21 ± 0.01
VIII	100 ± 15	0.38 ± 0.02
IX	45 ± 3	0.29 ± 0.02
X	32 ± 3	0.23 ± 0.04

(*) Means and standard-deviations for five determinations.

Table VI

Results for Cu and Co Analyses

Sample	Cu(*) (ppm)	Co(*) (ppm)
I	(**)	2.1 ± 0.1
II	67.7 ± 1.3	10.7 ± 1.0
III	38.9 ± 2.2	3.9 ± 0.3
IV	48.5 ± 2.0	1.8 ± 0.1
V	31.9 ± 0.9	6.2 ± 0.3
VI	37.9 ± 1.6	2.0 ± 0.1
VII	42.8 ± 1.4	7.0 ± 0.4
VIII	37.7 ± 1.1	0.7 ± 0.2
IX	21.0 ± 1.6	2.9 ± 0.3
X	12.2 ± 0.9	1.7 ± 0.1

(*) Means and standard-deviations for five determinations.
(**) Not detected.

Table VII

Results for the Lanthanides

Sample	Sm (ppm)	Eu (ppb)	Ce (ppm)	La (ppm)
I	0.21 ± 0.01	110 ± 3	0.58 ± 0.12	0.190 ± 0.005
II	0.24 ± 0.001	75 ± 6	1.42 ± 0.18	0.44 ± 0.02
III	0.042 ± 0.002	7 ± 1	0.22 ± 0.04	0.037 ± 0.005
IV	0.045 ± 0.002	17 ± 2	0.40 ± 0.04	0.21 ± 0.01
V	0.24 ± 0.02	67 ± 9	1.21 ± 0.19	0.30 ± 0.03
VI	0.25 ± 0.01	62 ± 2	1.54 ± 0.26	0.46 ± 0.02
VII	0.32 ± 0.01	100 ± 7	1.23 ± 0.16	0.37 ± 0.01
VIII	0.21 ± 0.01	66 ± 4	1.20 ± 0.09	0.69 ± 0.02
IX	0.27 ± 0.02	72 ± 10	2.13 ± 0.23	0.40 ± 0.02
X	0.29 ± 0.02	64 ± 8	1.50 ± 0.20	0.50 ± 0.04

All the Means and standard-deviations are for five determinations.

The determination limit for each element analysed was also calculated. This was made by using the irradiation conditions previously mentioned, and by assuming that the mass of the sample is of 100 mg. The determination limit (Lq) was calculated by the Currie's criterion[6], allowing a relative standard deviation of 10 %. The equation:

$$Lq = 50 \{ 1 + [1 + \frac{\mu_b}{12.5}]^{1/2} \}$$

where μ_b is the total background between the photopeak limits, was applied for the determination limit estimation.

Since manganese was analysed without chemical separation, the determination limit differs from sample to sample, because its value increases with the impurities concentration which may contribute to the Compton effect. On account of that, the determination limit for manganese was calculated for the best and the worst sample, taking into account the impurities concentration.

The sensitivity for lanthanides determination was not calculated because it depends on the relative concentration of the lanthanides present in the sample. The results for determination limits are shown in Table VIII.

Table VIII

Determination Limits of Some Elements

Element	Determination Limits
Mn	0.009% – 0.045%(*)
Fe	0.018%
Sc	9.3 ppb
Ca	0.07%
Cu	9.9 ppm
Co	1.5 ppm

(*) Range of determination limits.

DISCUSSION

The reproducibility of results obtained by the method presented in this paper is very good, what may be seen by the low standard-deviation values for the procedure, when it was performed with radioactive tracers added to inactive ore sample (Table II).

Since analytical results were corrected by means of the chemical separation yield values, it is reasonable to expect analytical results with a good accuracy.

The high sensitivity achieved for scandium, cobalt and copper determinations (Table III) arises from the chemical separation. The almost individual separation of the elements from the samples improved the sensitivity, because it allowed to use NaI(Tl) scintillation detector. Iron, for instance, might have been included in the copper-cobalt group, since it also forms a negatively charged complex in HCl medium. However, if iron had been included in the group, the gamma-ray spectrum

would have to be recorded by making use of a Ge-Li detector, since the energies values of the gamma-rays emited by ^{60}Co and ^{59}Fe are very similar. Taking into account the time required for iron separation and the much higher efficiency of the NaI(Tl) scintillation detector compared to that of the Ge-Li detector, the iron separation by solvent extraction, which is a very simple operation and allows the realization of several analyses simultaneously, was chosen.

Activation analysis is one of the best analytical techniques for manganese, as far as sensitivity is concerned. However, without chemical separation, the sensitivity may become very poor, as it may be seen from results shown in Table III.

Even though calcium and iron had been isolated from the sample, the results for these elements present a low sensitivity, because of their poor nuclear characteristics for activation analysis.

The main restriction concerning the application of activation analysis to magnesite ores comes from the ^{27}Mg activity ($T_{1/2} = 9.5$ min.), since it hinders the detection of impurities which, by irradiation with neutrons, give origin to short-lived radioisotopes.

Aluminum, for instance, was determined by Bodenlos[3,4] in all the magnesite samples. A rapid chemical separation of magnesium is not feasible, since the complete dissolution of a magnesite sample takes about 15-20 minutes, which is the time sufficient for the decay of many short-lived radioisotopes.

Even though the analytical procedure has been applied to magnesite samples, it may also be applied to other minerals of the calcite group (carbonates), subjected, obviously, to the suitable modifications which will be necessary for the matrix separation.

According to Bodenlos[3,4], the iron present in magnesite samples from the states of Ceará and Bahia may be due to pyrite found in the vicinity of the deposits.

However, investigations[7] about ion substitution in the crystalline structure, taking into account the ionic radii, show the possibility of magnesium substitution by iron II, in magnesite ores. At what concerns manganese, it difficult to found an explanation for its presence in magnesite ores, as it has already been stated by Bodenlos[3,4]. Copper, cobalt, scandium and the lanthanides were not analysed by Bodenlos[3,4] in magnesite ores, but the knowledge of their concentration may have an expressive meaning in the study of the origin of these deposits.

RESUMO

Desenvolveu-se um método para a análise de amostras de magnesita procedentes dos Estados do Ceará e da Bahia, usando a ativação com nêutrons térmicos. Analisam-se dez amostras.

A análise qualitativa indicou a presença de Mn, Fe, Sc, Ca, Cu, Co e alguns lantanídios.

O Mn foi analisado por análise por ativação sem separação química e os outros elementos foram analisados pela mesma técnica, depois da dissolução da amostra em HCl 8 M e seperação individual ou em grupos de elementos.

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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal, 11049 – Pinheiros
CEP 05508
01000 – São Paulo – SP

Telefone: 211-6011
Endereço Telegráfico – IEATOMICA
Telex – 011-23592 IENA BR