

Preconcentration of Molybdenum on Activated Carbon for the Analysis of Silicates Using the Injection Method in Flame Atomic Absorption Spectrometry

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Foi desenvolvido um procedimento analítico para a determinação de molibdênio em materiais geológicos silicatados por espectrometria de absorção atômica com chama (método de injeção), após sorção do complexo molibdênio-pirrolidinoditiocarbamato de amônio sobre carvão ativado. Foram estudados os efeitos do pH da amostra, da quantidade do reagente e do coletor e dos interferentes. O método foi aplicado para a análise de amostras de referência de rochas, intercomparação laboratorial e análise de amostras reais. O método mostrou-se ser simples e barato, fornecendo resultados precisos (RSD = 7%) e acurados. O limite de detecção foi calculado como sendo de $0.18 \mu\text{g g}^{-1}$. O método é aplicável à análise de amostras contendo níveis de molibdênio baixos, como $1 \mu\text{g g}^{-1}$.

An analytical procedure was developed for molybdenum determination in silicate geological materials by flame atomic absorption spectrometry (injection method), after sorption of the molybdenum-ammonium pyrrolidinedithiocarbamate complex on activated carbon. Sample pH, reagent and collector amounts and the presence of interfering species were studied. The method was applied to reference rock samples, interlaboratory comparison and real sample analysis. It is simple and cheap, and yields precise (RSD = 7%) and accurate results. The detection limit was determined to be $0.18 \mu\text{g g}^{-1}$. The procedure is applicable for the analysis of samples with molybdenum levels as low as $1 \mu\text{g g}^{-1}$.

Keywords: *molybdenum determination, activated carbon, rocks, injection method, atomic absorption spectrometry*

Introduction

Since its introduction in analytical chemistry, activated carbon has been used as a collector, permitting the determination and separation of low levels of analytes in several matrices, such as high-purity substances, water and rocks. Sorption on activated carbon from dissolved chemical species was studied for several elements. In most cases, suitable pH adjustment of the solution suffices¹⁻⁷. However, it was verified that in the presence of a chelating or precipitating agent, metal retention can be improved⁸. As such,

several trace metals have been determined by using xylenol orange⁹, sodium diethyldithiocarbamate^{10,11}, potassium ethyl xanthate¹¹⁻¹⁴, 8-hydroxyquinoline^{15,16}, dithiophosphoric acid O,O-diethyl ester^{17,18} and dithizone¹⁹ as complexing reagents. In addition, the species in its elemental state can be enriched on activated carbon²⁰. Van der Sloot *et al.*²¹ used ammonium pyrrolidinedithiocarbamate (APDC) as a complexing agent to enrich molybdenum from sea and surface waters (200 mL of sample). Monte and Curtius¹⁸ determined molybdenum in biological and geological materials using dithiophosphoric acid O,O-di-

ethyl ester as a complexing agent. Rocks with molybdenum contents within the 32–310 $\mu\text{g g}^{-1}$ and 2.4–34 $\mu\text{g g}^{-1}$ ranges were analyzed by FAAS and GFAAS, respectively.

Three approaches are commonly utilized for preconcentration or separation with activated carbon. Usually, a powdered portion of activated carbon is equilibrated with the sample, and thereafter filtered through a paper filter^{1,2,5-7,14,16}. Alternatively, the solution can be passed through a thin layer of activated carbon supported by a filtration device^{10-13,18,19}. These two procedures are preferred by most of the authors. Also, a small column packed with activated carbon has been used^{3,4}. Recently, this collector was successfully used in an on-line adsorption-elution flow system applied to copper determination in water²².

The mechanism of this sorption is still under investigation. Sigworth and Smith²³ studied the potential of activated carbons for the removal of inorganic compounds from water, and pointed out three mechanisms probably involved: a) physical adsorption due to the tremendous surface of activated carbons; b) ion-exchange due to the small number of oxygen complexes and other functional groups fixed on the carbon surface; and c) precipitation from a supersaturated solution induced by carbon through nucleation which reduces the solubility of a metallic salt. Also, colloidal suspensions can be broken up by setting the surface-charge structure which protects the colloidal particles. Also, powdered or granular carbon is an excellent filter.

Piperaki *et al.*²⁴ investigated nickel amino acid complexes and concluded that better sorption is attained with systems containing π -electrons and sulphur atoms. Chelates with ring structure, especially those of an aromatic nature, were found to be adsorbed for larger extent²⁵.

Molybdenum determination is very important in geological and geochemical studies due to its properties as pathfinder element in geochemical prospecting. Its determination by FAAS with a nitrous oxide-acetylene flame usually requires preconcentration techniques for analysis of samples with low molybdenum levels, such as rocks.

The injection method coupled with FAAS was introduced by Berndt and Jackwerth²⁶, and has some advantages when a preconcentration technique is needed for performing several analyses with low sample volumes.

In this work a simple method using APDC as the complexing agent to preconcentrate molybdenum from geological samples on activated carbon with FAAS as the detector is proposed. A small sample volume (200 μL) is required, since the injection technique is used.

Experimental

Apparatus and reagents

A Perkin Elmer model 403 atomic absorption spectrometer with an acetylene-nitrous oxide flame, connected

to a Perkin Elmer model 56 x-y recorder, was used. The wavelength was set at 313.3 nm and a 0.7 nm width slit was used. Manufacturer recommendations for maximum sensitivity were followed and fine adjustments in flame stoichiometry and the positions of the nebulizer and burner head were made. Ball mill grinders, Siebtechnik model TS 100 A (Germany) and Herzog HSM 100 A (Germany), equipped with tungsten carbide vessels were used in the preparation of rock samples. A 200 μL Eppendorf micropipet was used to inject the sample solution into the AAS nebulizer (injection method).

Solutions were prepared with distilled-deionized water and all reagents were of analytical grade. Acetylene and nitrous oxide (White Martins, Brazil) were of atomic absorption grade.

Molybdenum standard stock solution (1000 $\mu\text{g mL}^{-1}$) was prepared from Titrisol (Merck, Germany) by adequate dilution of the ampoule content. Analytical solutions of molybdenum were prepared from this solution by appropriated dilutions. The 1% (w/v) APDC (Sigma, USA) solution, prepared weekly, was stored in an amber bottle and kept in a refrigerator. Powdered activated carbon (Merck, Germany) was used without further purification. A 0.6% (w/v) activated carbon suspension was prepared immediately before use.

Preconcentration on activated carbon

In order to establish the analytical conditions for molybdenum determination in rock samples, a general procedure was investigated. APDC solution (10 mL) was added to the sample solution (50 mL) at pH 2 (adjusted with hydrochloric acid). Immediately after, 60 mg of activated carbon (10 mL suspension) was added and the mixture was stirred for 60 min. Thereafter, the mixture was filtered under vacuum through a 2.5 cm diameter paper filter (Whatman no. 40) placed on a glass filtering crucible. The filter with activated carbon was oven dried at 110 $^{\circ}\text{C}$ for 15 min. The activated carbon was then transferred to a PTFE beaker and digested with 2 mL of concentrated nitric acid in a sand bath at 120 $^{\circ}\text{C}$ until dry. The residue was dissolved in a small volume (1–5 mL) of 20% (v/v) nitric acid, and this solution was then injected into an AAS nebulizer. Alternatively, the solution could be passed through a thin layer of activated carbon (60 mg, supported by a 2.5 cm diameter filter paper placed on a glass filtering crucible) after the addition of the complexing agent (alternative procedure). For reasons explained in the Results and Discussion, the general procedure was used in all experiments and rock analyses.

Sample preparation

Reference rock samples and granite rocks were assayed. The reference rock samples (granite JB-1 from

Geological Survey of Japan - GSJ, and granite GH from Centre de Recherches Pétrographiques et Géochimiques, France) were used as received (powdered, 200-400 mesh). Granite rock samples from Piranhas (Goiás, Brazil) were broken and ground in a ball mill grinder until a fine powder (150 - 200 mesh) was obtained. The procedure for chemical decomposition involved an acid treatment^{27,28}: 0.5-5 g of the powdered sample was treated in a PTFE beaker with 15 mL of 48% hydrofluoric acid, and the mixture was allowed to stand for about 1 h. Then, the beaker was heated in a sand bath (150 °C) until dryness. After cooling, 15 mL of a mixture of concentrated nitric and perchloric acids (3 + 1 v/v) was added and heated in the same sand bath until dry. The residue was then treated with 2.5 mL of concentrated hydrochloric acid, water and 4 drops of 30% hydrogen peroxyde under gentle warming to achieve complete solubility. After filling the volume up to 50 mL, the pH was adjusted to 2. This solution was used in the preconcentration step.

Atomic absorption measurements

The injection method²⁶ was chosen to introduce 200 μL of the analytical and sample solutions into the AAS nebulizer. Molybdenum analytical solutions (2 mL) in the 10 to 50 $\mu\text{g mL}^{-1}$ range were preconcentrated in the same way as the samples by the general preconcentration procedure described above. Peak height was used as analytical parameter, in all measurements.

Results and Discussion

Influence of chemical variables in the preconcentration step

In order to define the conditions for molybdenum preconcentration from real samples, several tests were run to optimize sample acidity and the amounts of APDC and activated carbon. Analytical solutions (10 mL) with 100 μg of molybdenum and a pH ranging from 1 to 8 (adjusted with hydrochloric acid or ammonium hydroxide) were analyzed after the general preconcentration procedure. Higher absorption signals were obtained for solutions with pH values between 1 and 2.5. Above 2.5, a sharp decrease in the signal was observed, and no signal was observed for solutions with $\text{pH} > 4$. Therefore, it was decided to work at pH 2.

An amount of APDC was tested within the 40-200 mg range by using solutions (10 mL) with 100 μg of molybdenum at pH 2. Above 50 mg of APDC, the signal was constant and variations in the amount of the complexing agent did not affect the signal. However, for amounts < 50 mg, the signal decreased slowly with the reduction of the amount of APDC, emphasizing the relevance of the chelating agent. In fact, tests carried out without APDC showed recoveries 50% lower than the values obtained in the presence of APDC, which demonstrates the need for this re-

agent. In order to ensure good recoveries and considering that rocks were to be analyzed, it was decided to work with 100 mg of APDC per sample in the preconcentration step.

The quantities of the collector were also investigated. Several tests were run with 25 to 100 mg of activated carbon using solutions containing 100 μg of molybdenum (10 mL). Between 50 and 100 mg, the amount of collector did not affect the absorbance signals. For preconcentrations performed with less than 50 mg of activated carbon, lower recoveries were obtained due to a small loss of collector during its transfer, or to the lower efficiency of collection. Therefore, the amount of collector was selected at 60 mg.

For the dissolution of activated carbon in the preconcentration step, nitric, hydrochloric and sulphuric acids were assayed. All tests were performed with 20% (v/v) solutions, and the best results were obtained in a nitric acid medium. Hydrochloric and sulphuric acids showed recoveries of 70% and 40% relative to that achieved with nitric acid. The nitric acid concentration was further investigated between 10 and 50% (v/v), and the best results were observed with 20%, which was then chosen for this work.

Effect of interfering species in the preconcentration

With the aim of assessing the selectivity, several species were studied. These species were chosen after considering their presence as major and minor components in silicate rocks and the possibility of reaction with the chelating agent or of provoking flame interference during the preconcentration and determination steps, respectively. The amounts of interfering species used in this study depended on their concentrations in the silicate rocks and on the aliquot taken in the sample dissolution step. Table 1 shows the results. Iron (III), calcium, manganese (II), aluminum, titanium, magnesium, sodium and potassium do not interfere. Also, when the species studied are together in the same solution in their highest amounts, the signal obtained did not differ from that when a solution containing only molybdenum was used.

Experimental conditions for FAAS

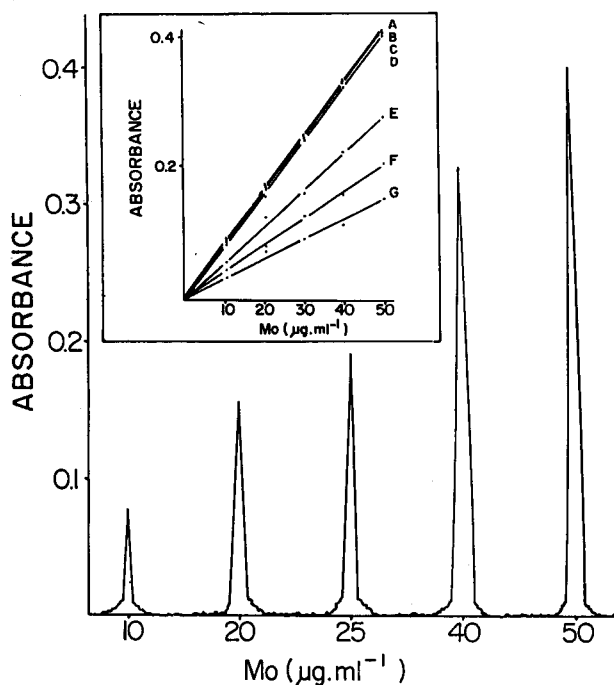
Some of the instrumental conditions for molybdenum determination were studied. As the signal of molybdenum is greatly influenced by acetylene-nitrous oxide flame stoichiometry, assays were made to ensure better sensitivity. The best conditions were established with a rich lean flame. The volume used in the injection method was also studied by injecting 20 to 1000 μL of solution with molybdenum within the 10 to 50 $\mu\text{g mL}^{-1}$ range in 20% (v/v) nitric acid. The results shown in Fig. 1 indicate that injection volumes of 200 to 1000 μL give the same signals compared to those obtained through direct aspiration measurements. In order to permit higher replication and minimal time consumption, injection volumes of 200 μL were chosen.

Table 1. Effect of concomitant species after pre-concentration on activated carbon. Mass of Mo, 20 μg ; injection method, 200 μL .

Species	Mass of concomitant (μg)	Ratio of concomitant to Mo ($\mu\text{g}/\mu\text{g}$)	Relative Mo signal
Mo	0	-	1.00
Fe (III)	500	25	0.98
	2000	100	0.96
	5000	250	1.06
	10000	500	1.07
	20000	1000	1.07
Ca	250	12.5	0.97
	1000	50	0.98
	2000	100	1.04
	5000	250	1.04
Mn (II)	80	4	1.04
	800	40	1.07
	2000	100	1.07
Al	5000	250	1.07
	25000	1250	1.08
Ti	200	10	1.04
	5000	250	1.04
K	160	8	1.03
	4000	200	1.04
Na	160	8	1.07
	4000	200	1.08
Mg	200	10	1.04
	5000	250	1.06
Fe (III)	20000	1000	1.03
Ca	5000	250	
Mn (II)	2000	100	
Al	25000	1250	
Ti	5000	250	
K	4000	200	
Na	4000	200	
Mg	500	250	

Analytical figures of the merits of the pre-concentration and determination of molybdenum

The performance of the general procedure was better than the alternative procedure (described in the "Experimental" section) in relation to reproducibility, accuracy and recovery for molybdenum determination. The recoveries

**Figure 1.** Typical calibration peaks obtained with the injection method (using 200 μL). Analytical curves obtained with (A) continuous aspiration and injected volumes of (B) 1000 μL ; (C) 500 μL ; (D) 200 μL ; (E) 100 μL ; (F) 50 μL and (G) 20 μL .

were better than 90% with a RSD of 7% for $n = 5$. Analytical curves show good linearity within the range of 10-50 $\mu\text{g mL}^{-1}$ ($A = 0.001 + 8 \times 10^{-3} [\text{Mo } (\mu\text{g mL}^{-1})]$), with a correlation coefficient better than 0.998. The characteristic concentration (related to 1% of absorption) was 0.6 $\mu\text{g mL}^{-1}$, which agrees very well with the literature²⁹. The detection limit (3σ) was found to be 0.18 $\mu\text{g mL}^{-1}$. The pre-concentration factors depend on the amount of sample taken in the decomposition step and the final acid volume after sorption on activated carbon. They were sufficient to analyze rocks containing molybdenum levels as low as

Table 2. Results obtained for reference rock samples from GSJ, and intercomparison analysis with CRPG. Values in $\mu\text{g Mo g}^{-1}$.

Sample	Found values ^a	Certified values ^b	CRPG values
JB - 1	33.5 \pm 0.7	35	-
GH	3.1 \pm 0.1	3	-
PIR - 1	286 \pm 10	-	290
PIR - 2	15.1 \pm 0.6	-	15.1
PIR - 9	3.1 \pm 0.2	-	3.1
PIR - 26	6.0 \pm 0.3	-	5.8
PIR - 47	2.0 \pm 0.1	-	1.8

a = Mean of triplicate analysis. b = Data obtained from Ref. 30.

Table 3. Results obtained for some granite rocks from Piranhas (Goiás, Brazil), by the proposed method and chemical composition. Data in % of major and minor components, and in $\mu\text{g g}^{-1}$ for molybdenum.

Component	Samples					
	PIR-1	PIR-2	PIR-26	PIR-42	PIR-44	PIR- 46
SiO ₂	76.55	66.85	75.18	72.92	74.40	70.98
TiO ₂	0.04	0.12	0.28	0.30	0.33	0.45
Al ₂ O ₃	12.11	12.92	12.14	13.01	12.99	13.96
Fe ₂ O ₃	0.15	0.41	0.85	0.91	0.87	0.82
FeO	0.62	0.77	1.20	1.39	1.10	1.77
MnO	0.01	0.02	0.02	0.02	0.03	0.03
MgO	0.11	0.01	0.18	0.41	0.63	0.60
CaO	0.54	0.31	0.79	1.11	0.91	1.09
Na ₂ O	3.72	5.93	3.58	3.96	3.23	3.27
K ₂ O	5.88	9.66	5.23	4.69	4.75	5.35
P ₂ O ₅	0.01	0.03	0.07	0.01	0.06	0.09
L.O.I. ^a	0.46	1.20	0.52	0.62	0.69	0.64
Mo	286 ± 10	15.1 ± 0.6	6.0 ± 0.3	4.0 ± 0.3	1.0 ± 0.1	1.0 ± 0.1

a = loss on ignition.

$1 \mu\text{g g}^{-1}$. The matrix effect on the atomic absorption molybdenum signal is highly decreased with the preconcentration step. The 4% reproducibility for the proposed method was obtained by preconcentrating twelve solutions containing $20 \mu\text{g}$ of molybdenum. To assess the accuracy, both reference rock samples and intercomparison laboratory analysis were used. Two granite reference rock samples were analyzed and the results are shown in the Table 2. Also, five granite rock samples were analyzed by ICP/AES in the laboratories of the Centre de Recherches Pétrographiques et Géochimiques - CRPG, France and the results are also shown in Table 2. Both results obtained were in good agreement with the certified³⁰ and CRPG values.

Application to real samples

The granite occurrence near the city of Piranhas, in the state of Goiás, Brazil, was studied due to its geochemical properties, and some samples were analyzed with the goal of observing possible molybdenum anomalies. Fifty granite samples were analyzed for major and minor elements, and molybdenum was determined with the proposed method. The chemical composition of some of these rocks is shown in Table 3. Only one sample (PIR-1) shows high molybdenum concentration demonstrating a punctual mineralized region. A comparison between the proposed method and those previously^{18,25} reported for the determination of molybdenum after preconcentration on activated carbon reveals some differences. This method, in spite of

its relatively low detection limit, could be applied to a wide range of rocks. The interference problems are minimized by using low pH in the preconcentration step making the chelation of molybdenum more selective.

In conclusion, the developed method could be applied to rock analysis with low molybdenum levels (as low as $1 \mu\text{g g}^{-1}$), with good precision and accuracy, using relatively simple and inexpensive reagents and apparatus.

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