QUÍMICA ANALÍTICA (1997) 16 [Suppl 1]:S61-S67

QUÍMICA ANALÍTICA
Elsevier Prensa S.A. 1997

Chemical modifiers for the determination of chromium in marbles by electrothermal atomic absorption spectrometry

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Received December, 29th, 1995 / Accepted June, 5th, 1996

Summary: The determination of chromium in calcium-rich material, such as marble, has been studied. Platinum and rhodium (as chlorides) were examined as chemical modifiers and their efficiency was tested on the determination of chromium in a marble reference material. In the absence of modifiers, the pyrolysis temperature was 1200°C, whereas when 1 μg Pt or Rh were present, this temperature was increased to 1350°C. Quantification was performed with matrix-matched standards. Accurate results and good agreement with the certified value were found in the presence of rhodium or platinum. The effect of the chemical modifiers on the calcium matrix of marble has been investigated by molecular absorption measurements. It was found that rhodium and platinum probably promote the volatilization of calcium matrix (probably as $CaCl_{(g)}$) early at the pyrolysis step, before the atomization of chromium. Since other chloride-containing compounds, such as sodium chloride, did not promote the early volatilization of the calcium matrix, it was concluded that this effect is element-specific for platinum and rhodium compounds.

Key words: Chromium determination, electrothermal atomic absorption spectrometry, chemical modifiers, analysis of marble

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Introduction

The determination of Cr in various geological materials has been accomplished with various techniques, such as ETAAS [1], instrumental neutron-activation analysis (INAA), inductively coupled plasma atomic-emission spectrometry (ICP-AES) and X-ray fluorescence spectrometry (XRF) [2]. The determination of trace elements in marbles is used for the characterization of ancient marble artefacts [3,4] and various techniques have been used for these determinations, including INAA [3,5], ICP-MS [4] and XRF [6]. Nevertheless, sensitive multielement techniques are still quite expensive for many laboratories, such as ICP-MS, or demand special laboratory requirements, such as INAA. Therefore, electrothermal atomization atomic absorption methods are of great interest.

Electrothermal Atomization Atomic Absorption Spectrometry (ETAAS) is widely used for the determination of chromium in μg l^{-1} levels in various matrices. However, the determination of Cr is considered difficult due to the severe interferences, preatomization losses and decreased sensitivity, which occur in complex matrices, as in the case of geological samples [7]. In addition, the background correction is not complete with instruments equipped with the deuterium-arc background corrector. Attempts to solve these problems lead to the development of many procedures,

from which the most widely applied is chemical modification [1, 8-12]. Since methods which evade matrix separation or preconcentration are preferable, to avoid contamination, chemical modification methods are of a great importance. The most widely used chemical modifier is magnesium nitrate [9,10]. Tungsten was also used for the determination of Cr in water samples [8]. Recently, several metals were compared as possible chemical modifiers for the determination of Cr in environmental and biological samples and it was found that platinum and rhodium gave the best results [11,12].

The aim of this study was to investigate the determination of Cr in an alkaline-earth rich material, such as marble. Chemical modification, with Pt and Rh, proved to be essential. Chromium was examined as one of several candidate trace constituents, appropriate for identifying the origin of marbles obtained from various ancient monuments and objects. This work was undertaken in the frame of a wider investigation of the determination of trace metals in marbles.

Experimental

Instrumentation

A Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with a HGA 400 graphite furnace was used for the atomic absorption measurements at the 357.9 nm resonance line of Cr with a 0.7 nm spectral band width. The Cr hollow-cathode lamp was employed as radiation source and operated at 18 mA. Pyrolytically coated graphite tubes (Perkin-Elmer Part No. B0135653) were used throughout the study. A 20-µl volume of the solutions was dispensed in the graphite tubes with an AS-1 autosampler and an Eppendorf micropipette with disposable polypropylene tips. Tungsten-halogen light source was used for background correction (the background absorbance level was ranged from 0.1 to 0.3 depending on the sample). The graphite furnace operating conditions are summarised in Table 1.

The time-resolved atomic absorption pulses were recorded with an IBM compatible PC Quest 286/16 computer using a home-made program. This system is described elsewhere [13].

Reagents

All chemicals used in this study were of analytical grade. All glass and polypropylene ware were kept in 10% v/v HNO_3 for at least one night and then rinsed with 1% v/v HNO_3 three times and subsequently ten times with distilled de-ionized water before use. The acids were of Suprapur grade (Merck, Germany). Chromium standards were prepared by diluting a 1 $g \cdot l^{-1}$ Cr (as $CrCl_3$) stock solution (Titrisol, Merck) with distilled de-ionized water and acidified to a final HNO_3 concentration of 1% v/v. Modifiers stock solutions were prepared by dissolving appropriate amounts of their salts in acid media and diluting to a final volume with water. The modifiers studied were Rh and Pt (as chlorides).

Determination of Cr in marble

Approximately 0.2 g of the powdered marble was accurately weighed, dissolved with the minimum volume (about 0.5 ml) of a warm mixture of concentrated nitric acid and hydrochloric acid (2+1) and diluted with water to a final volume of 10.0 ml. An aliquot of 500 µl of this solution was diluted 1+1 with distilled de-ionized water or the solution of the modifier containing the appropriate amount of it. The temperature programme in Table 1 was followed. The quantification was performed with a matrix-matched standard curve prepared by spiking with 0, 2.0, 5.0, 7.0 and 10.0 $\mu g l^{-1}$ of Cr in 1.00 ml of diluted marble solution. The accuracy was tested analyzing a Marble Reference Material (MRM) with a certified Cr value of 2.647±0.018 $\mu g \cdot g^{-1}$ [5].

Effect of modifiers on the calcium matrix

The mechanism of the action of the modifiers on the calcium matrix of the marble was investigated by molecular absorption measurements, in the range of 350 - 650 nm, using the tungsten-halogen lamp as radiation source with a slit bandwidth of 0.14 nm and by atomic absorption measurements in the 239.9 nm wavelength of calcium using a hollow-cathode lamp of Ca as the radiation source. The molecular absorption measurements were carried out point by point with manual wavelength setting. The same temperature programme, as in Table 1, was followed, except that the vaporization temperature of the calcium matrix was 2200°C.

Results and Discussion

Determination of Cr in Marbles

The samples used are dolomites and have approximately the following composition: 39% m/m CaO, 20%

Table 1. Temperature programme for the determination of Cr in marbles.

Step	Temperature/°C	Ramp time /s	Hold time/s	Ar flow rate/ml min^{-1}	Read
Drying	120	10	20	300	
Pyrolysis	Variable*	10	20	300	
Atomization	2400	1	6	0	ON
Cleaning	2650	1	3	300	

*Variable: T_{pyr} was 1200°C without modifiers, 1350°C with 1 µg Pt or 1 µg Rh.

m/m MgO, 50-500 mgg^{-1} Fe_2O_3 and very low content of Al_2O_3 and SiO_2 [3]. It is shown in figure 1a that irregular peaks were obtained for Cr in the absence of modifiers. The tungsten-halogen lamp, used here for the background correction, did not compensate for the high background signal of the sample effectively, since the maximum pyrolysis temperature, which could be used without losses of Cr, was 1200°C. When 1 µg of Pt was used as a chemical modifier, the background signal was reduced (Fig. 1b) and the sample could be pyrolysed at 1350°C without loss of the sensitivity (Fig. 2). The same was observed in the presence of 1 µg of Rh. Ramp atomization mode at 2400°C was used instead of maximum power atomization, due to the background correction problems in the latter case. The same problem for Cr was observed by Halls and Fell [14] and Berndt and Sopczak [15] who proposed that ramp atomization mode at 2400°C eliminated the interference.

The recovery results of chromium added to marble sample with and without chemical modification are summarized in Table 2. The data demonstrate that quantitative recovery was obtained only in the presence of Rh or Pt. This was confirmed by the analysis of a marble reference material and marble samples which have been previously analyzed by instrumental neutron activation analysis (INAA) [3]. The results are presented in Table 3 and show that accurate results obtained only in the presence of Rh and Pt.

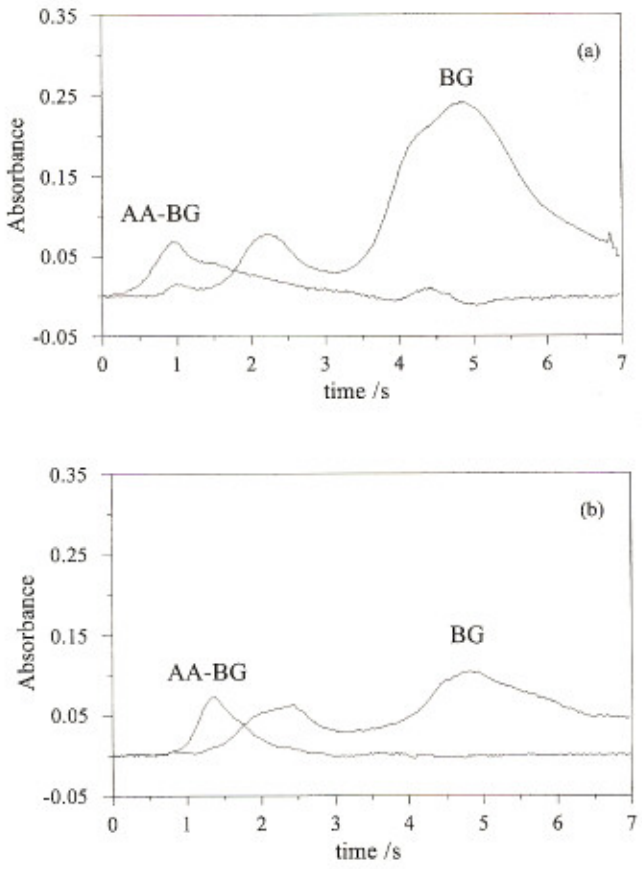

Figure 1. Atomic absorption signals of chromium (AA(BG) and non-specific absorption (BG) of the marble in the absence (a) and in the presence (b) of 1 µg of Pt.

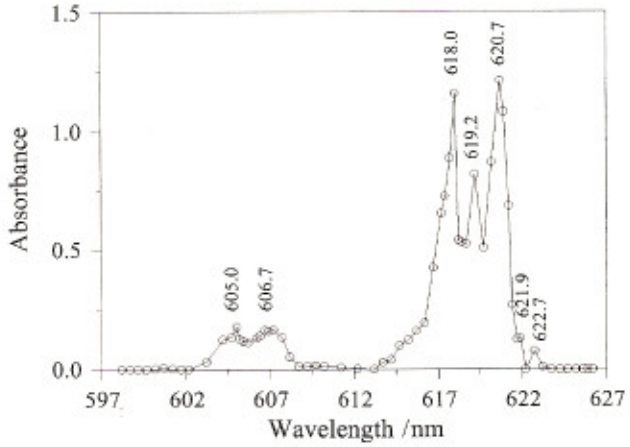

Figure 2. Effect of the pyrolysis temperature on the atomic absorption of chromium (A,B) and the non(specific absorption (C,D) of a marble sample spiked with 5 μgl^{-1} Cr in the absence (A,C) and in the presence (B,D) of 1 µg of Pt.

The characteristic masses m_o in the absence of a chemical modifier, as well as in the presence of 1 µg Rh or 1 µg Pt were 4.9 pg, 4.0 pg and 4.2 pg, respectively, using integrated absorbance measurements. These m_o values are about 30% higher than the m_o values derived from aqueous solution in a previous study [11]. The corresponding relative standard deviations of seven replicate measurements (within-run) for a total Cr content of 4.5 μgl^{-1} were 2.0%, 2.2% and 2.5%, respectively.

The decreased sensitivity of Cr determination in the marble can be attributed to the recondensation of the matrix particles at the cooler ends of the graphite tube, trapping the analyte in the same region, subsequently leading to decreased analytical signal [16,17]. This was further confirmed from the accumulation of a white solid substrate on the surface of the graphite tube, especially at the tube ends, after successive injections of marble solutions. This resulted in a decrease of sensitivity (by about 30%) and deterioration of reproducibility (from 2.0% to 15%). After about 30 successive atomization cycles, cleaning of the surface with tissue paper was essential for continuing the measurements.

Table 2. Recovery of chromium added to marble with and without chemical modifiers

Without modifiers			with 1 μg Pt		with 1 μg Rh	
Cr added(μg l^{-1})	Cr found (μg l^{-1})	Recovery (%)	Cr found (μg l^{-1})	Recovery (%)	Cr found (μg l^{-1})	Recovery (%)
0.0	1.96		2.60		2.46	
2.0	4.32	118.0	4.59	99.5	4.58	106.0
5.0	7.58	112.4	7.56	99.2	7.52	101.2
7.0	9.46	107.2	9.60	100.0	9.39	99.0
10.0	12.56	106.0	12.61	100.1	12.40	99.4
Mean Recovery (%) :		110.9		99.7		101.4

Table 3. Determination of chromium in marble samples. The results are given as the mean value of n determinations ± the standard deviation.

	Cr (μg g^{-1})			
	without modifiers	with 1 μg Pt	with 1 μg Rh	INAA [3]
MRM[a] (n=4)	2.33±0.18	2.69±0.04	2.54±0.08	2.6±0.2
Sample 1 (n=2)	0.20 , 0.19	0.26 , 0.25	0.26 , 0.27	0.24±0.02
Sample 2 (n=2)	0.67 , 0.70	0.77 , 0.78	0.79 , 0.78	0.78±0.01
Sample 3 (n=2)	0.37 , 0.41	0.44 , 0.42	0.48 , 0.46	0.45±0.02

[a] MRM: Marble Reference Material with a certified value of 2.647±0.018 μg g^{-1} [5].

Effect of modifiers on the calcium matrix

The decrease of the background signal from the marble matrix in the presence of platinum prompted us to investigate the effect of platinum on the atomic absorption signal of calcium. The atomic absorption signal (both height and area) was increased about 30 % and was shifted to earlier time. This means that the atomization of calcium in the presence of platinum was more efficient and followed an easier path. Since the chloride salts of the modifiers were introduced in the graphite tube among with the sample, it was assumed that calcium chloride was produced. Therefore, the molecular absorbance of 5 μg $CaCl_2$ was investigated in the range of 590-630 nm. The resulting molecular spectrum is shown in fig. 3. The strong peaks at 618.0, 619.2 620.7 and 619.7 nm are associated with $CaCl_{(g)}$, whereas the peaks at 605.0, 606.7 nm can be ascribed to calcium oxide [18,19]. These peaks were not observed in an empty atomizer or when solutions of the modifiers (Pt and Rh) were injected. In addition, in order to ascertain that these peaks were due to calcium containing species, we have measured the absorption signals with increasing amounts of Ca and a linear correlation has been observed between absorbance and calcium mass at all the characteristic wavelengths (620.7, 618.0 and 605.0 nm). Furthermore, when 100 μg of $Ca(NO_3)_2$ were introduced into the graphite tube, very small signals were obtained at the above-mentioned wavelengths. When $RhCl_3$ or K_2PtCl_4 were introduced with $Ca(NO_3)_2$ the signals were greatly enhanced, which means that CaCl was certainly formed. The same was also observed with other chloride salts, such as NaCl. Hence, most of the marble matrix (consisted mainly by

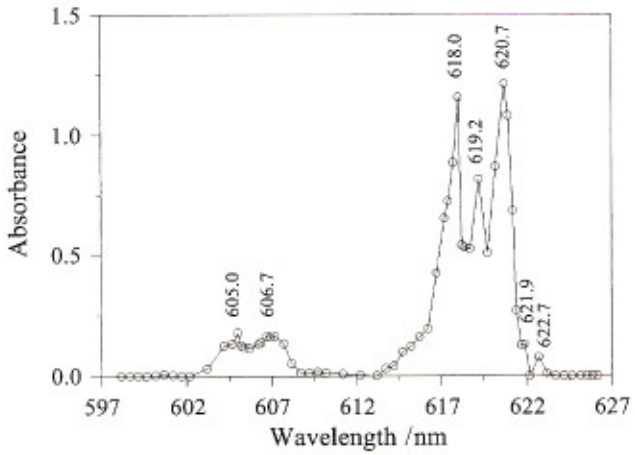

Figure 3. Molecular absorption spectrum measured during the vaporization of 5 μg $CaCl_2$ (Tpyr=1000°C and Tvap=2200°C).

CaO) was converted to calcium chloride in the presence of chloride ions.

We have further investigated whether the signal observed was due to scattering from particles. We have found that this signal did not follow the wavelength-dependence observed in other studies [16] but it was wavelength-specific. Therefore, we assumed that the peaks observed in the spectrum presented in fig. 3 were due to calcium species.

In the presence of Pt or Rh modifiers, the molecular absorption signal of CaCl was decreased substantially, as it is shown in fig.4. We have also studied the effect of pyrolysis and vaporization temperature on the signal at 620.7 nm and the results are presented in fig. 5. This figure shows that, in the absence of modifiers, enough of the calcium matrix remained in the graphite at high pyrolysis temperature and was released during the atomization of Cr (fig.5A,B). In the presence of 1 μg of Pt, a large portion of the calcium matrix was removed early at the pyrolysis temperature (fig. 5C,D). The same trends were observed in the presence 1 μg of Rh. In another experiment, 100 μg of $Ca(NO_3)_2$ were vaporized and the observed molecular absorbance signal (measured at 605.0 nm), was stable up to a T_{pyr} of 1400°C and it increased with increasing vaporization temperature up to a T_{vap} of 2600°C. On the other hand, in the presence of Pt or Rh, calcium chloride was formed and it was removed from the furnace early at the pyrolysis step. The remaining molecular absorbance of calcium species reached a maximum at vaporization temperature of 1800°C and then decreased gradually with a further increase in the vaporization temperature. It may be concluded from these results that calcium matrix was vaporized during chromium atomization in the absence of modifiers. In the presence of Pt or Rh a large amount of this matrix was removed from the tube early at the pyrolysis step and the remaining matrix was vaporized at temperatures lower than the atomization temperature of Cr.

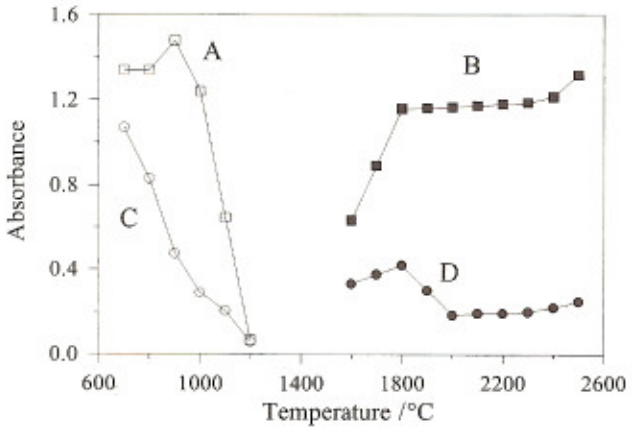

Figure 5. Effect of pyrolysis temperature (hollow symbols) and vaporization temperature (full symbols) on the molecular absorbance signal of 5 μg $CaCl_2$ (620.7 nm) without (A,B) and with 1 μg of Pt (C,D).

In order to investigate whether the modification effect can be attributed to platinum or to chloride ions, 1.4 μg of NaCl, were injected with $CaCl_2$ in the furnace. It was observed that the molecular absorbance of CaCl did not changed at T_{pyr}=1000°C, as shown in fig.6. This means that only Pt or Rh chloride promote the early removal of $CaCl_2$ (as $CaCl_{(g)}$) and not other common chloride salts.

Therefore, the decrease in the background signal can only be attributed to the modification effect of Pt and Rh chloride modifiers. It is likely that Pt and Rh not

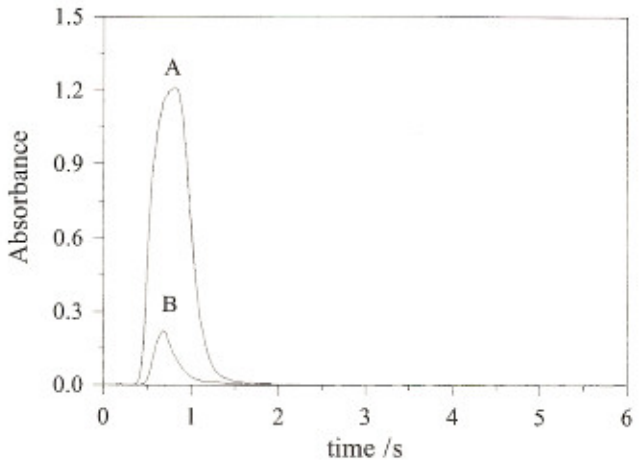

Figure 4. Molecular absorption signals (λ=620.7 nm) from the vaporization of 5 μg $CaCl_2$ at a T_{pyr}=1000°C and a T_{vap}=2200°C, (A) without and (B) with 1 μg of Pt.

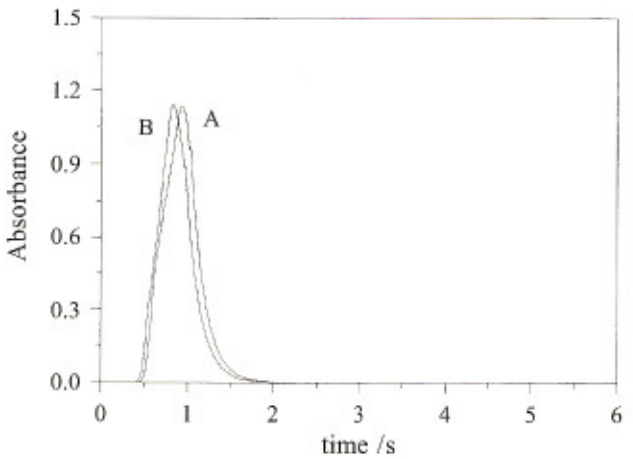

Figure 6. Molecular absorption signals (λ=620.7 nm) from the vaporization of 5 μg $CaCl_2$ at a T_{pyr}=1000°C and a T_{vap}=2400°C, (A) without and (B) with 1.2 μg NaCl.

only stabilize chromium species, but also assist the removal of part of the calcium matrix during the pyrolysis step and prior the atomization of Cr. The residue of the non-specific absorbance signal can be attributed to other refractory oxides which are vaporized during the atomization step. This signal is small enough to be easily corrected by the background correction system of the instrument.

Conclusions

Matrix interferences were observed in the determination of chromium in the inorganic matrix, of marble. Accurate results were obtained only in the presence of platinum or rhodium as chemical modifiers, since pyrolysis temperature could be increased up to 1350°C and the background signal was reduced significantly. Platinum and rhodium promoted the volatilization and the removal of calcium matrix early at the pyrolysis step, and the remaining of the background signal could be easily corrected.

Acknowledgements

The authors are indebted to Dr. J. Maniatis, and Dr. V. Mandi, N.C.S.R. "Demokritos", Athens, for kindly supplying the marble reference material and marble samples. One of the authors (N. Thomaidis) would like to thank the Greek State Scholarships Foundation for financial support of this work.

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