

## Effects of Alkali and Alkaline Earth Metal Chlorides on the Atomization of Lead and Chromium in Graphite Furnace Atomic Absorption Spectrometry

S. BEKTAS\* and S. AKMAN†\*\*

\*Hacettepe University, Department of Chemistry, 06532 Beytepe, Ankara, Turkey

\*\*Istanbul Technical University, Department of Chemistry, 80626 Maslak, Istanbul, Turkey

Potassium chloride, calcium chloride, sodium chloride and magnesium chloride cause many different types of interference in the determination of lead and chromium by graphite furnace atomic absorption spectrometry. Simultaneous volatilization of the analyte and the interferent from different, but close, points in the tube are very helpful in the explanation of interference mechanisms. The kind of interference that affects the sensitivity of the determination depends on the thermal behavior of the matrix before and during atomization of the elements. If chloride vapor is formed by decomposition of the matrix before or during atomization of the analyte elements, the formation of a metal chloride in the gas phase may be responsible for decreasing in the sensitivity. If, on the other hand, the matrix is present as a solid or liquid while the elements atomize, the occlusion of the analyte in the bulk of the matrix and the loss by a carrier-type mechanism or a slower transfer of heat to the analyte delaying the atomization cause some changes in the sensitivity. Expulsion of analyte vapors by expanding matrix gases was not effective due to the low heating-rate of the system used.

**Keywords** Graphite furnace atomic absorption spectrometry, interferences, lead and chromium atomization

Matrix interference in graphite furnace atomic absorption spectrometry has been widely studied since this method became popular in the early 1970s and the literature is full of reports on problems of different origin.

Reports were made on the volatility of a chromium compound that led to substantial losses during thermal pretreatment in a furnace.<sup>1</sup> Nevertheless, other authors were unable to find volatile chromium compounds.<sup>2</sup>

There are reports in the literature on relatively strong interference due to chloride<sup>3,4</sup>, as well, which could not be verified by other authors.<sup>5</sup> Frech *et al.*<sup>6</sup> stated that a thermal pretreatment stage in a graphite tube must be considered as a potential source for chromium losses (particularly when chlorine is present), since gaseous chromium oxychloride,  $\text{CrO}_2\text{Cl}_2(\text{g})$ , may be formed. They stated that since gaseous chromium oxychloride was stable at temperatures up to 1200°C there is a risk for losses of chromium at intermediate temperatures.  $\text{CrCl}_2(\text{s})$ , on the other hand, was present on the tube surface between 1300–1700°C. Chromium is known to form stable metallic carbides<sup>7</sup>, and this has been reported to be the reason for the incomplete volatilization of chromium from graphite tubes.<sup>8</sup> The formation of the chromium carbide has been mentioned by many

workers.<sup>6,9,10</sup>

Lead is a very popular element in graphite furnace atomic absorption spectrometry. Many publications on the determination of lead in various samples reported numerous types of interference. Ottaway<sup>11</sup> reported a considerable signal depression due to chlorides and observed the spectrum of lead chloride. He concluded that lead is volatilized in molecular form. Czobik and Matousek<sup>12</sup> referred to the carrier effect that leads to simultaneous volatilization of, for example, sodium chloride and lead; sodium chloride can volatilize in microgram quantities at temperature slightly above 700°C and can carry lead with it. These authors established that in the presence of sodium chloride the lead signal virtually coincides with the volatilization of sodium chloride from the tube wall. Yasuda and Kakiyama<sup>13,14</sup> assumed that elements such as cadmium, lead and zinc form gaseous metal chlorides in the presence of higher chloride concentrations and that these are partially transported from the tube at the start of atomization. They observed the spectra of numerous metal halides at relatively low temperatures which, however, did not appear at higher temperatures. Smeyers-Verbeke *et al.*<sup>15</sup> found that alkaline-earth-chlorides can lead to losses of the analyte element during a thermal pretreatment. They reported that through a careful choice of the thermal pretreatment

† To whom correspondence should be addressed.

program, the interferent could be removed and the interference thus reduced or eliminated. Fuller<sup>16</sup> found substantial differences for the interference of magnesium chloride on the determination of lead depending on the graphite surface. While strong interference could be observed in new uncoated tubes and in pyrocoated tubes, no interference was observed in aged tubes. The interference due to magnesium chloride could be eliminated by the addition of oxalic acid. Both oxalic acid and finely dispersed carbon in aged tubes reduce lead oxide to metallic lead. Fuller thus concluded that the interference due to magnesium chloride is a vapor-phase interference. Many authors<sup>17-19</sup> suggested that the graphite surface played an important role and affected the atomization and interference mechanisms for lead. These mechanisms may be affected by the presence of reagents such as nitrates and by the oxygen released from the nitrate decomposition.<sup>19-21</sup> Frech and Cedergren<sup>22</sup> were able to show for the determination of lead in steel that in the absence of hydrogen, volatile lead chlorides are formed at 400°C, leading to losses during thermal pretreatment. In the presence of sufficiently large quantity of hydrogen, chlorine is expelled from the graphite tube at 600°C as hydrogen chloride. If, on the other hand, the sample is present in a nitric acid solution and a relatively high thermal pretreatment temperature is not applied, the partial pressure of oxygen during atomization can be quite large. Gaseous lead oxides can then be formed, leading to a loss in sensitivity.<sup>23</sup> One of the main causes for vapor-phase interferences in graphite furnaces is the formation of monohalides. A shift of the dissociation equilibrium through decomposition products of the solvent or the matrix, is a further important factor. Even small quantities of gaseous chlorine cause a redistribution of lead in the gas phase so that it is present as the volatile monochloride PbCl and dichloride PbCl<sub>2</sub>.<sup>22</sup> These forms are mostly expelled with the purge gas, so that substantial losses of lead occur. In the presence of hydrogen, on the other hand, high chloride concentrations can be tolerated before noticeable quantities of lead chlorides are formed. According to Frech and Cedergren<sup>23</sup>, in an isothermal furnace, interference should hardly occur for the determination of lead in the presence of higher concentrations of sodium chloride. Sodium chloride is a relatively stable molecule and the partial pressure of chlorine is low. Pb(g) is the preferred species above 1200°C and PbCl<sub>2</sub>(g) only occurs in larger quantities below 900°C. Nevertheless, it should be emphasized that these conditions are valid only for an isothermal furnace. Slavin and coworkers<sup>24,25</sup> have pointed out that at least some of the previously described matrix interference due to chlorides actually losses represented of the analyte element in the form of the volatile chlorides during thermal pretreatment. Nevertheless, they could not rule out vapor-phase interferences, since the bond energies of gaseous metal halides are very large and complete dissociation may not occur. This

was confirmed by Siemer *et al.*<sup>26</sup> who showed that the signal suppression for lead in the presence of iron chloride could be reduced when the analyte vapor was observed in a zone of higher temperature. Welz *et al.*<sup>27</sup>, who tested the integrated response for lead in nickel chloride and sodium chloride using "dual-cavity platform", found that in spite of the substantially different physical and chemical properties of the two chlorides, the interference appeared, in general, to proceed by the same mechanisms. No evidence could be found for a gas-phase reaction interference. Lead chloride was formed in the condensed phase and lost in the form of gaseous molecules during thermal pretreatment or early in the atomization stage. Expulsion of the analyte from the furnace together with the very rapidly expanding gases due to the fast heating rate applied during the atomization stage was a very important type interference.

In our previous paper<sup>28</sup> the effects of sodium chloride, calcium chloride and magnesium chloride on the atomization behavior of manganese and cadmium were examined and volatilization of the analyte element and the interferent from separate points of the graphite tube has been proved useful in providing more information on the interference mechanisms. It was pointed out that if a near-coincidence in appearance times of analyte and matrix atoms existed, gas-phase interference can be expected. If, on the other hand, the matrix was still in the condensed phase during atomization of the analyte, occlusion of the element in the matrix and loss by carrier mechanism was quite possible.

In this work, the effects of potassium chloride, calcium chloride, sodium chloride and magnesium chloride on the atomization behavior of lead and chromium were examined by the interpretation of the thermal pretreatment temperature curves obtained for "the analyte alone", "the analyte in the matrix" and "the matrix alone" together with their physical and chemical properties. In addition, the pipetting of the analyte and the matrix separately onto the different, but close, points of the tube helped to explain of the effects of the matrix on the atomization of the analyte.

## Experimental

A Perkin-Elmer Model 400 atomic absorption spectrometer equipped with a HGA-74 graphite furnace and a continuum source background corrector was used throughout this work. The absorbances were read as peak height from a Perkin-Elmer Model 56 recorder. Lead determinations were carried out with a hollow cathode lamp operated at 8 mA at the 283.3-nm line and a spectral band width of 0.7 nm. Chromium, determinations were carried out with a hollow cathode lamp operated at 10 mA at the 357.8 nm and a spectral band width of 0.2 nm. The 1000 ppm stock solutions of the elements of interest were prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> in 1% HNO<sub>3</sub> and Cr metal rod in minimum

volume of concentrated HCl and were diluted to volume. Stock matrix solutions (10%w/v) were prepared from NaCl, KCl, CaCl<sub>2</sub>·2H<sub>2</sub>O and MgCl<sub>2</sub>·6H<sub>2</sub>O salts. All of the chemicals were of analytical reagent grade and were not further purified. Test solutions were diluted daily to appropriate concentrations with freshly distilled deionized water. Aliquots of 20 µl of 0.5 ppm lead reference solution (1×10<sup>-8</sup> g), and 0.06 ppm chromium reference solution (1.2×10<sup>-9</sup> g) were used throughout the work. Twenty microliters of 1%w/v potassium, calcium and sodium chlorides (2×10<sup>-4</sup> g) and 20 µl of 6%w/v of magnesium chloride (1.2×10<sup>-3</sup> g) were used unless otherwise stated. All solutions were introduced with a Finn pipet and the injection hole was enlarged to facilitate sample pipetting onto the separate points of graphite tube. Drops of solutions onto the surface were controlled by using a mirror to be sure not to mix with each other. In the case of mixing during the drying step, the program was stopped, the tube was cleaned by applying maximum heating and the procedure was repeated. The operating parameters of graphite furnace are given in Table 1.

The change of temperature with time in the atomization step was calibrated with an optical pyrometer. Nitrogen was used as purge gas and the graphite tubes were uncoated. All data points given in this work are averages of several repetitions on different days using different tubes. A background corrector was always operated during all determinations.

Table 1 Operating parameters for HGA-74 furnace

Parameter	Steps			
	1	2	3	4
Temp./°C	100	variable	2300 (Pb) 2700 (Cr)	2700
Time/s	30	20	12	5
Internal flow rate/ml min <sup>-1</sup>	300	30	0	300

## Results and Discussion

Non-spectral matrix interference could be due to several different processes:<sup>27</sup> (i) a condensed-phase reaction between the analyte and matrix and the formation of a compound which is volatilized and carried out of the absorption volume without being atomized; (ii) a gas-phase interference, *i.e.* a reaction between analyte atoms and matrix atoms or radicals to form gaseous molecules of different thermostability; (iii) occlusion of the analyte in the bulk of the matrix and loss by a carrier mechanism; (iv) expulsion of the analyte vapor together with rapidly expanding matrix gases.

Table 2 shows the absorbance values obtained from separated and mixed pipetting of the analyte and interferent together with the analyte alone. Separate volatilization of the analyte and interferent from different, but close, spots in the graphite tube has been very informative for a better understanding of interference mechanisms. This arrangement allows independent volatilization of the analyte element and the interferent which do not come into contact in the condensed phase. It can be expected that volatilized species mix readily in the gas-phase so that interference due to gas-phase interactions (*i.e.* mechanisms (ii) and (iv)) remain essentially the same when the analyte and interferent are mixed or separated. Condensed phase interactions (*i.e.* mechanisms (i) and (iii)) must disappear when the analyte and interferent meet only in the gas-phase, though. Consequently, in the case of mechanisms (i) and (iii), which require intimate contact between analyte and interferent in the condensed phase, different sensitivities should be obtained for mixed and separated pipetting of the analyte and interferent. If, on the other hand, the same sensitivity loss is obtained for both mixed and separated solutions, which means the interference is independent whether the analyte and interferent are mixed or not, then only alternatives (ii) and (iv) should be taken into account. If (1)=(3)±(2) in

Table 2 Effects of separate volatilization of the analyte element and interferent from different but close points in the tube center

Element	Interferent	Relative absorbances of <sup>a</sup>		
		analyte alone (1)	analyte mixed with matrix (2)	analyte and matrix separately pipetted (3)
Pb	KCl	1.00±0.02	0.89±0.03	1.01±0.05
Pb	CaCl <sub>2</sub>	1.00±0.02	0.64±0.05	0.98±0.07
Pb	NaCl	1.00±0.02	0.54±0.03	0.67±0.06
Pb	MgCl <sub>2</sub>	1.00±0.02	0.47±0.03	0.97±0.05
Cr	KCl	1.00±0.03	0.82±0.05	0.81±0.05
Cr	CaCl <sub>2</sub>	1.00±0.03	0.75±0.05	0.77±0.05
Cr	NaCl	1.00±0.03	0.80±0.05	0.82±0.05
Cr	MgCl <sub>2</sub>	1.00±0.03	1.10±0.03	0.98±0.05

a. The average of many repetitive absorbance values was accepted 1.00 for the sake of simplicity and the average of absorbances obtained from other experiments, (2) and (3), were relative values with respect to the average of analyte alone. All the experimental conditions are as given in the experimental section. Thermal pretreatment temperature is 300°C.

Table 2, alternatives (i) and (iii) come into consideration, e.g. Pb in KCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>, and Cr in MgCl<sub>2</sub>. If (2)=(3)±(1) then (ii) as well as (iv) can be predicted, e.g. Cr in KCl, CaCl<sub>2</sub> and NaCl. If (1)=(2)±(3) then all the alternatives should be considered, e.g. Pb in NaCl. A clear distinction between possible interference mechanisms is frequently difficult and sometimes impossible. The predictions should be supported by further experiments. More detailed information could be obtained from the interpretation of the thermal pretreatment graphs given below.

#### Effects of potassium chloride

The influence of the thermal pretreatment temperature on the atomization signal for lead alone in the presence of a 20000-fold excess of potassium chloride and non-specific absorbance from potassium chloride at the lead wavelength are depicted in Fig. 1(a). Essentially, the behavior of molecular absorption vs. temperature curves does not change with wavelength in all figures; we only used the ones obtained at the lead wavelength. An examination of the plots reveals that lead signals are a little affected by the matrix. The loss of potassium chloride begins at about 500°C; it almost completely leaves the furnace at 900°C for a pretreatment time of 20 s. The atomization temperature of potassium taken as its chloride was found to be about 1300°C.<sup>29</sup> Accordingly, the reason for the loss of potassium chloride at lower temperatures should be the removal of the salt as molecular vapor, rather than thermal decomposition to its atoms. The appearance of potassium and chlorine atoms in the gas phase is possible only after 1300°C, whereas the atomization temperature of lead in the matrix is 800°C; even when the peak maximum of lead is reached, there are still no free chlorine atoms present in the gas phase. One can, therefore, not expect that the lead and chlorine atoms will combine in the gas phase to depress the lead atomic absorption signal. Table 2 is consistent with this proposal. The formation of lead chloride in the condensed phase during the pretreatment step, which is

volatilized and carried out of absorption volume, seems to be unlikely because removal of lead as volatile lead chloride during pretreatment step should have been increased proportionally with the pretreatment temperature as well as time. In an additional set of experiments, it was observed that the duration of the pretreatment step did not affect the "lead in potassium chloride" signal. Both "lead alone" and "lead in potassium chloride" curves are stable up to 800°C and in fact a little increase was observed for lead mixed with potassium chloride after 600°C. This shows that there is no lead loss during the pretreatment step in the presence of potassium chloride; thus a condensed phase reaction can be excluded. Lead may be occluded as its molecular or atomic form and carried in potassium chloride clusters during the atomization step *i.e.* mechanism (iii). Figure 1 supports this idea because occlusion should be independent of the thermal pretreatment temperature as long as the matrix does not vaporize and (as shown in the figure), "lead in potassium chloride" curve does not change below 600°C. An increase in the thermal pretreatment curve for "lead mixed with potassium chloride" between 600–800°C is due to the removal of some potassium chloride during the pretreatment step; a smaller amount of interferent is left in the tube to carry lead atoms in the atomization step. The data given in Table 2 is in good agreement with this proposal. Alternative (iv), *i.e.* expulsion of the analyte vapor together with rapidly expanding matrix gases which was proposed by many workers<sup>27,30</sup> seems to be ineffective, or negligible in our conditions because if it had occurred, absorption due to separate pipetting of the analyte and matrix would have been affected to a some degree when compared with lead alone; but, it did not. The reason for this discrepancy is quite clear. The HGA-74 graphite furnace used in this work has a low heating rate which decreases the analyte vapor expulsion from the furnace together with rapidly expanding matrix gases. On the other hand, this mechanism is very effective due to the very fast heating rates used in those systems.

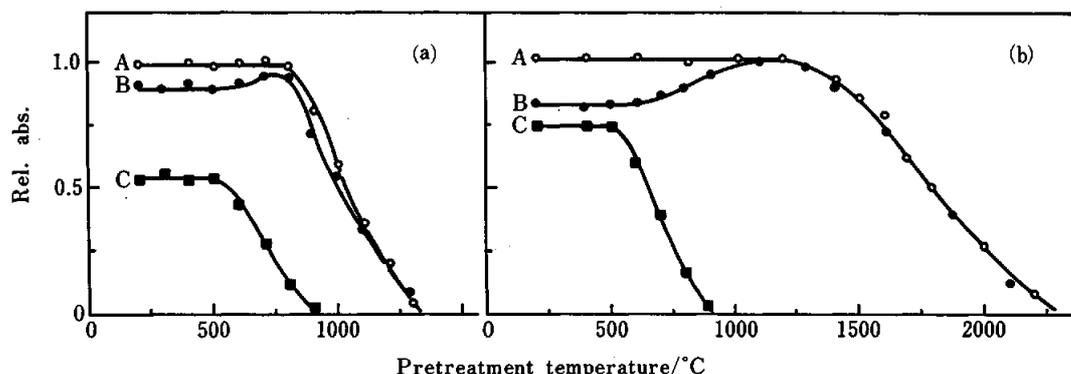


Fig. 1 Thermal pretreatment temperature graphs for (a) lead, (b) chromium: A, analyte alone (lead 10 ng, chromium 1.2 ng); B, analyte mixed with 0.2 mg KCl; C, 0.2 mg KCl background absorbance.

For the effects of potassium chloride on chromium, the curves in Fig. 1(b) can be easily explained in terms of the thermal properties of chromium and potassium chloride. As explained before, potassium chloride atomizes at 1300°C although it vaporizes at lower temperatures as the molecular form. The atomization temperature of chromium in potassium chloride was found to be 1350°C. Consequently, a near coincidence in the appearance times of chromium and chlorine atoms makes a gas-phase reaction possible to form a molecule, *i.e.* mechanism(ii). Table 2 strongly supports this mechanism. The atomic absorption potassium signal taken with a potassium hollow cathode lamp for  $2 \times 10^{-4}$  g KCl under the conditions used for lead or chromium atomization actually remains at a high level over an extended period of time, which suggests a flow of potassium or chlorine atoms causing the expulsion of analyte vapor from the tube as well as formation of a molecule in the gas-phase. Analyte vapor expulsion from the furnace together with vaporization matrix (alternative (iv)) should be considered whenever a near coincidence in appearance times of analyte and matrix exists. Table 2 and Fig. 1(b) are not in disagreement with this mechanism. Table 2, on the other hand, makes condensed-phase interference impossible, so the condensed-phase reaction between the analyte element and the interferent to form a volatile compound during thermal pretreatment step or occlusion of analyte in the matrix, *i.e.* mechanisms (i) and (iii) can be eliminated. When the thermal pretreatment temperature is adjusted to a value higher than 600°C, potassium chloride, which causes interference in the atomization step, is partly removed from the furnace and the chromium signals are partly restored; finally, at thermal pretreatment temperatures above 1100°C, reach to "chromium alone" value because there is no potassium chloride left in the tube to cause any interference during atomization. It is important to note that although the shapes of the curves in Figs. 1(a) and (b) are alike, their causes are completely different. We have discussed all

of the alternatives for potassium chloride in detail; from now on, the possible alternatives for other interferents will be more briefly discussed, unless a situation not mentioned occurs.

#### Effects of calcium chloride

Figure 2(a) shows the effect of calcium chloride on lead absorbance. The thermal behavior of calcium chloride is similar to that of potassium chloride. The atomization temperature of calcium, taken as chloride, was found to be 1550°C.<sup>29</sup> However, the calcium chloride thermal pretreatment curve starts decreasing at about 800°C, far below the atomization temperature. These losses should be due to the vaporization of calcium chloride in a thermal pretreatment step, like potassium chloride. The hydrolysis of calcium chloride can form calcium oxide, CaO, which may be responsible from the decrease in the calcium chlorides signal; however, the transfer of CaO to the vapor phase can not be expected because CaO is known to be an involatile substance ( $t_{bp}=2850^\circ\text{C}$ ).<sup>31</sup> The gaseous chlorine atoms from calcium chloride can only be present above 1550°C, a temperature too high even for the peak maximum of "lead mixed with calcium chloride" absorption signal. In this situation no gas-phase reaction, *i.e.* alternative (ii), can be expected. Table 2 strongly supports the absence of a gas-phase reaction. From the data in Table 2, only a condensed-phase effect can be expected. Therefore, the expulsion of lead atoms with a rapidly expanding matrix, alternative (iv), can be easily eliminated as well. If it were possible, separate injection would be affected from this interference.<sup>27,30</sup> From the curves in Fig. 2(a), the formation of volatile lead chloride in a condensed phase, alternative (i), seems to be unlikely because signal depression is independent of the pretreatment temperature before the vaporization of calcium chloride; moreover, in an additional set of experiments the duration of the pretreatment step did not affect the signal. In this situation, the most possible mechanism seems to be occlusion.

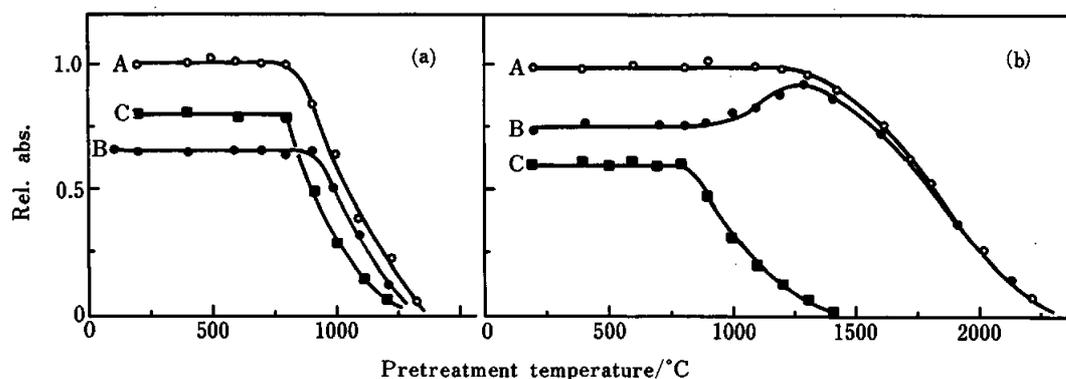


Fig. 2 Thermal pretreatment temperature graphs for (a) lead, (b) chromium: A, analyte alone (lead 10 ng, chromium 1.2 ng); B, analyte mixed with 0.2 mg CaCl<sub>2</sub>; C, 0.2 mg CaCl<sub>2</sub> background absorbance.

An examination of the curves in Fig. 2(b), which are quite similar to that of "chromium in potassium chloride" (Fig. 1(b)), again indicates a depressive effect of calcium chloride on the chromium absorbance. From the previous discussion, we have known that free gaseous chlorine atoms will be formed after 1550°C, a temperature which is quite close to the atomization temperature of chromium. Therefore, if the thermal pretreatment temperature is adjusted to below 800°C, then during the atomization step, starting from about 800°C, the matrix will evaporate rapidly and a small amount of residue (may be not at all) will be left on the graphite surface while chromium atomizes. Because of the simultaneous existence of chromium and chlorine atoms in the vapor phase, the resulting gas-phase reaction to form a molecule is most probable. After a pre-atomization temperature of 1400°C, the interfering matrix leaves the furnace, restoring the signal to its original value. The data in Table 2 are in good agreement with a gas-phase reaction. Nevertheless, the probability of expulsion of the analyte from the furnace together with expanding matrix gases (or its decomposition products) should also be taken into consideration. The atomic absorption signal of calcium obtained from the atomization of  $2 \times 10^{-4}$  g of calcium chloride actually remains at a high level over an extended period of time, suggesting a flow of calcium as well as chlorine atoms, causing the rapid expulsion of chromium from the absorption volume. Alternatives (i) and (iii), *i.e.* a condensed-phase reaction and occlusion, seems to be unlikely according to the explanations made for other situations. Since gas-phase reaction and expulsion mechanisms can not be distinguished from each other due to the similarity of evidence, expulsion has had to be proposed (and will be done) whenever a gas-phase reaction is likely, or *vice versa*. Nevertheless, we do not believe the expulsion mechanism to be so effective, because of the slow heating rate of HGA-74. Alternatives (i) and (iii) *i.e.* a condensed-phase reaction and occlusion seem to be unlikely, according to the Table 2, and explanations given before.

#### Effects of sodium chloride

As shown in Fig. 3, even though sodium chloride molecules enter the vapor phase above 700°C, the atomization temperature of sodium taken as its chloride was found to be above 1000°C, *i.e.* NaCl decomposes to its atoms above 1000°C.<sup>29</sup> The appearance of sodium and chlorine atoms coincides with that of lead atoms; thus, a gas-phase reaction as well as expulsion of lead from the furnace can be expected. The atomic absorption signal of sodium obtained from the atomization of  $2 \times 10^{-4}$  g NaCl under the conditions used for lead and chromium remains at a high level over the atomization step, which suggests a flow of sodium and chlorine atoms causing expulsion and gas-phase reactions. The data in Table 2 are inconsistent with this idea. From Table 2, condensed-phase interference is possible as well. This can not be the formation of a

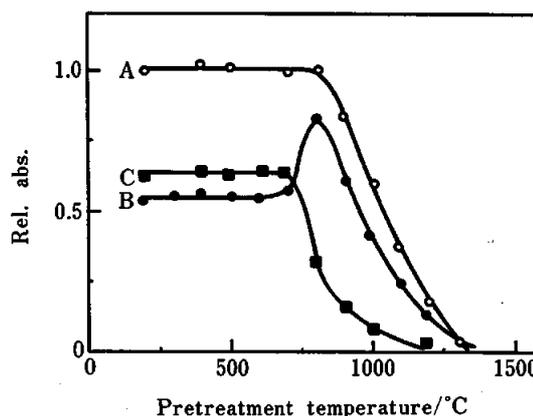


Fig. 3 Thermal pretreatment temperature graphs for A, 10 ng lead alone; B, 10 ng lead mixed with 0.2 mg NaCl background absorbance.

volatile compound in the condensed phase which is carried out of the furnace during the pretreatment step for the reasons previously given. Therefore, in addition to a gas-phase reaction and expulsion, an occlusion mechanism which is in agreement with the data in Table 2 and Fig. 3 and is consistent with the results of Czobik and Matousek<sup>12</sup>, can be expected. From the data in Table 2, it can be concluded that the effect of occlusion is much more important than gas-phase effects, namely gas-phase reaction and expulsion. In similar work by Welz *et al.*<sup>27</sup>, no evidence could be found for a gas-phase reaction under their experimental conditions. Actually, this is not surprising since they used an STPF (standard temperature platform furnace) technique with a very rapid heating rate in pyrolytic tubes. In the STPF technique, which provides a constant and much higher gas-phase temperature, gas-phase reactions are considerably reduced or completely eliminated, so that the formation of lead chloride in the gas-phase may not be expected under their conditions; in our case, however, with slow heating rated HGA-74 furnaces, it is not an unexpected situation to observe a gas-phase reaction. In addition, in their work, expulsion of lead from the furnace together with rapidly expanding matrix gases, which are directly dependent on the heating rate, was the leading interference due to the ultra-fast heating rate. In our system, on the other hand, the heating rate is so slow that an effective expulsion mechanism can not be expected. Consequently, the results and discussion presented for this work disagree with theirs because the experimental conditions are completely different. Since the effect of sodium chloride in chromium is the same as that of potassium chloride and calcium chloride on chromium, it will not be dealt with further.

#### Effects of magnesium chloride

Magnesium chloride stays on a graphite surface up to higher temperatures, as presented by the decomposition curve of magnesium chloride in Fig. 4(a). Thermogravi-

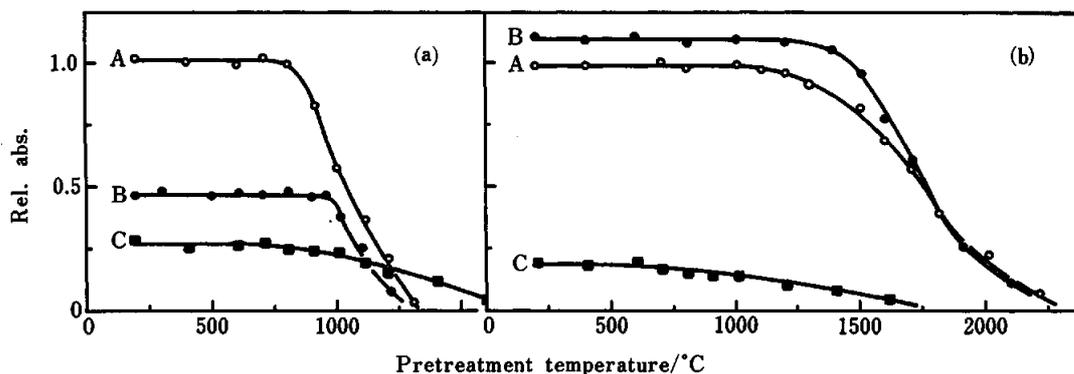
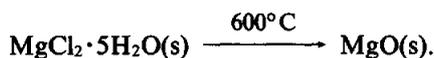


Fig. 4 Thermal pretreatment temperature graphs for (a) lead, (b) chromium: A, analyte alone (lead 10 ng, chromium 1.2 ng); B, analyte mixed with 1.2 mg  $\text{MgCl}_2$ ; C, 1.2 mg  $\text{MgCl}_2$  background absorbance.

metric analysis<sup>15,16</sup> indicates that  $\text{MgO}$  is a common intermediate in the decomposition of the chloride,



Therefore, magnesium chloride will be active as magnesium oxide, a substance that is not easily volatilized ( $t_{\text{mp}}=2800^\circ\text{C}$ ,  $t_{\text{bp}}=3600^\circ\text{C}$ ).<sup>31</sup> It will thus present on a graphite surface while lead atomizes, and physically (*i.e.* occlusion), suppress the atomic lead signal. Since there is no source for the formation of chloride atoms to react with lead atoms in the gas-phase during the atomization stage, one can not account for a gas-phase reaction. The data in Table 2 support this suggestion. In contrast to the matrix examples studied before, Fig. 4(b) shows a small positive effect of magnesium chloride on chromium absorbance. Because of the presence of  $\text{MgO}$  on a graphite surface during the atomization of chromium, physical interference in the condensed phase must be considered. The physical interference of the matrix may reveal two competitive mechanisms, one of which is the suppression of the atomic signal by the occlusion of the analyte in the matrix. The other mechanism which may cause an increase in the sensitivity is that  $\text{MgO}$  decreases the contact of the analyte with the tube surface, like a platform action, so that atomization is delayed until the tube wall and gas-phase have reacted their final temperature and are in equilibrium. This may increase the atomization efficiency due to the higher gas-phase temperature and decrease the possibility of carbide formation between the analyte and graphite as well. It can be concluded that, in the case of chromium, the increasing effect is obviously dominant. Likewise, for the determination of copper and iron in matrices of higher concentrations, Slovak and Docekal<sup>32</sup> reported that a matrix can act as a "mini-platform" delaying atomization and, thus, increasing the sensitivity. Slavin *et al.*<sup>33</sup> recommended magnesium nitrate, which actually does not behave differently from magnesium chloride, as an especially effective reagent for matrix modification.

In another paper<sup>34</sup> they reported that the function of the  $\text{Mg}$  addition is to imbed the analyte in a matrix of  $\text{Mg}$  oxide, delaying vaporization of the analyte until the  $\text{Mg}$  oxide is vaporized.

## References

1. D. Behne, P. Brotter, H. Gessner, G. Hube, W. Mertz and U. Rosik, *Fresenius' Z. Anal. Chem.*, **278**, 269 (1976).
2. G. R. Sirota and J. F. Uthe, *Anal. Chem.*, **49**, 823 (1977).
3. K. Julshawn, *At. Absorption Newsl.*, **16**, 149 (1977).
4. K. Matsusaki, T. Yoshino and Y. Yamamoto, *Anal. Chim. Acta*, **124**, 163 (1981).
5. J. Kumpulainen, *Anal. Chim. Acta*, **113**, 355 (1980).
6. W. Frech, E. Lundberg and A. Cedergren, *Prog. Anal. At. Spectrosc.*, **8**, 257 (1985).
7. I. Rubeska, J. Koreckova and D. Weiss, *At. Absorption Newsl.*, **16**, 1 (1977).
8. C. Veillon, K. Y. Patterson and N. A. Bryden, *Anal. Chim. Acta*, **136**, 233 (1982).
9. C. Veillon, B. E. Guthrie and W. R. Wolf, *Anal. Chem.*, **52**, 457 (1980).
10. W. Wendl and G. Muller-Vogt, *Spectrochim. Acta*, **39B**, 238 (1984).
11. J. M. Ottaway, *Proc. Analyt. Div. Chem. Soc.*, **13**, 185 (1976).
12. E. J. Czobik and J. P. Matousek, *Talanta*, **24**, 573 (1977).
13. S. Yasuda and H. Kakiyama, *Anal. Chim. Acta*, **84**, 291 (1976).
14. S. Yamada and H. Kakiyama, *Anal. Chim. Acta*, **89**, 369 (1977).
15. J. Smeyers-Verbeke, Y. Michotte, P. van den Winkel and D. L. Massort, *Anal. Chem.*, **48**, 125 (1976).
16. C. W. Fuller, *At. Absorption Newsl.*, **14**, 73 (1975).
17. W. G. Brumbaugh and S. R. Koirtiyohann, *Anal. Chem.*, **60**, 1051 (1988).
18. J. P. Erspamer and T. M. Niemczyk, *Anal. Chem.*, **54**, 538 (1982).
19. R. E. Sturgeon, D. F. Mitchell and S. S. Berman, *Anal. Chem.*, **55**, 1059 (1983).
20. J. A. Holcombe, G. D. Rayson and N. Akerlind,

- Spectrochim. Acta*, **37B**, 319 (1982).
21. A. Cedergren, W. Frech and E. Lundberg, *Anal. Chem.* **56**, 1382 (1984).
  22. W. Frech and A. Cedergren, *Anal. Chim. Acta*, **131**, 45 (1976).
  23. W. Frech and A. Cedergren, *Anal. Chim. Acta*, **88**, 57 (1977).
  24. W. Slavin, G. R. Carnrick and D. C. Manning, *Anal. Chem.*, **56**, 163 (1984).
  25. D. C. Manning and W. Slavin, *Appl. Spectrosc.*, **37**, 1 (1983).
  26. D. D. Siemer, E. Lundberg and W. Frech, *Appl. Spectrosc.*, **38**, 389 (1984).
  27. B. Welz, S. Akman and G. Schlemmer, *J. Anal. At. Spectrom.*, **2**, 793 (1987).
  28. S. Bektas, S. Akman and T. Balkis, *Anal. Sci.*, **5**, 438 (1989).
  29. B. V. L'vov, *Spectrochim. Acta*, **33B**, 153 (1978).
  30. B. Welz, S. Akman and G. Schlemmer, *Analyst* [London], **110**, 459 (1985).
  31. R. C. Weast, "*Handbook of Chemistry of Physics*", 61st ed., CRC Press, Boca Raton, 1980.
  32. Z. Slovak and B. Docekal, *Anal. Chim. Acta*, **130**, 203 (1981).
  33. W. Slavin, D. C. Manning and G. R. Carnrick, *At. Spectrosc.*, **2**, 136 (1981).
  34. W. Slavin, G. R. Carnrick and D. C. Manning, *Anal. Chem.*, **54**, 621 (1982).

(Received October 16, 1989)

(Accepted February 5, 1990)