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Effect of Chloride Ion on Lead Signal Appearance in the Co-Existence of Iron in Electrothermal Graphite Furnace Atomic Absorption Spectrometry

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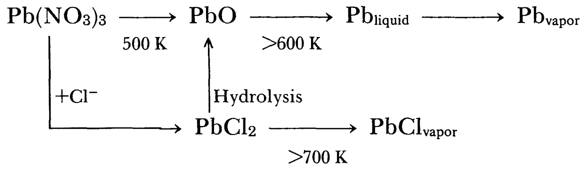
The atomic absorption signals for lead were measured in various chloride matrices at a charring temperature of 700 K. A typical double-peak signal was observed with iron(III) chloride, while a single peak was observed with iron(III) nitrate. At a charring temperature of 1440 K, the first peak disappeared and only the second peak remained; the atomization temperature of the latter was in agreement with that in the iron matrix. The larger content of the chloride ion increased the first peak absorption and decreased the second peak absorption without any shift of the peak temperatures, showing that one species for the second peak was converted to the same species for the first peak by the addition of a chloride ion. The appearance temperature of the first peak signal in the X^-–Fe^{3+} matrix system increased in the order $Cl^- < Br^- < I^-$. It was concluded that the appearance of the first peak is caused by the dissociation of lead halide.

Although graphite furnace atomic absorption spectrometry (GFAAS) is favorable for an analysis of a trace amount of lead, severe matrix interference[1,2] decrease its sensitivity by diversifying the mechanism of metal vapor formation. The mechanism of interference elimination has been discussed from the viewpoint of kinetics.[1]

The chloride ion is one of the most unfavorable matrices, because of the formation of volatile lead chloride. Wendl and Müller-Vogt[2] investigated the reaction of lead in a chloride matrix by X-ray diffraction and molecular absorption for PbCl, and proposed the following reaction processes:



This mechanism shows that interference from chlorides is caused by volatilization of lead chloride at a temperature lower than that required to decompose the compound on the graphite surface. Frech and Cedergren[3–5] also concluded from a high-temperature gas-phase equilibrium calculation that the formation of the volatile lead chlorides, such as $PbCl_2$ and PbCl, should result in decreasing the signal of lead.

L'vov et al.[6] reported the appearance of double-peak signals of lead in sodium chloride. They considered that the second peak was caused by a revolatilization of lead condensed with a matrix on the cooler outer ends of the furnace tube. McLaren and Wheeler[7] also reported the appearance of double-peak signals in the ascorbic acid matrix, which resulted from the formation of the massicot and litharge dimorphic forms of PbO in a furnace. Salmon et al.[8] also proposed that the double-peak signal for lead was caused by two major types of active sites which chemisorbed oxygen on the graphite tube.

It was also found in this work that a double-peak signal for lead appeared in the presence of iron(III) chloride; that the chloride ion was responsible for the appearance of the first peak and that the iron caused each peak to shift to the higher temperature side; and that two different types of atomization mechanisms might exist. The mechanism that caused the appearance of the first peak is discussed in the present paper.

Experimental

Apparatus and Materials. A Hitachi Model Z-8000 flame and graphite furnace atomic absorption spectrometer equipped with a Zeemann-effect background corrector and an optical temperature controller was used. The term of the maximum heating mode was defined as the mode of maximum heating feasible with the optical temperature controller used in the present work. The sample was injected by an automatic sampler. The peak height and area were automatically printed out and displayed using a Hitachi Data Processor. The time-absorbance signals sent to an OKI Model if-800 personal computer through RS-232C could also be stored on a diskette at 20 ms intervals. The temperature of the graphite tube was recorded at 4 ms intervals using the optical temperature controller; its analog output data were converted to digital data and stored on a diskette using an OKI personal computer. The temperature was calibrated using a CHINO Model IR-AH1S radiation thermometer with a radiation factor of one.

The standard instrumental conditions were 120 °C (setting) and 30 s for the drying stage, 800 K, ramp time 20 s and hold time 5 s for the charring, 2700 K, ramp time 0 s and hold time 2 s for the atomizing. The reproducibility of the atomization temperature for the nonpyrolytic graphite (NPG) tube was 0.3% at 1419 K (n=10). When the maximum heating mode was used, the heating rates were 1450 K s^{-1} for the NPG tube and 1200 K s^{-1} for pyrolytic graphite (PG). Coating of the NPG tube with iron oxide was carried out by charring 20 μl of an iron(III) nitrate solution (1000 mg l^{-1} of

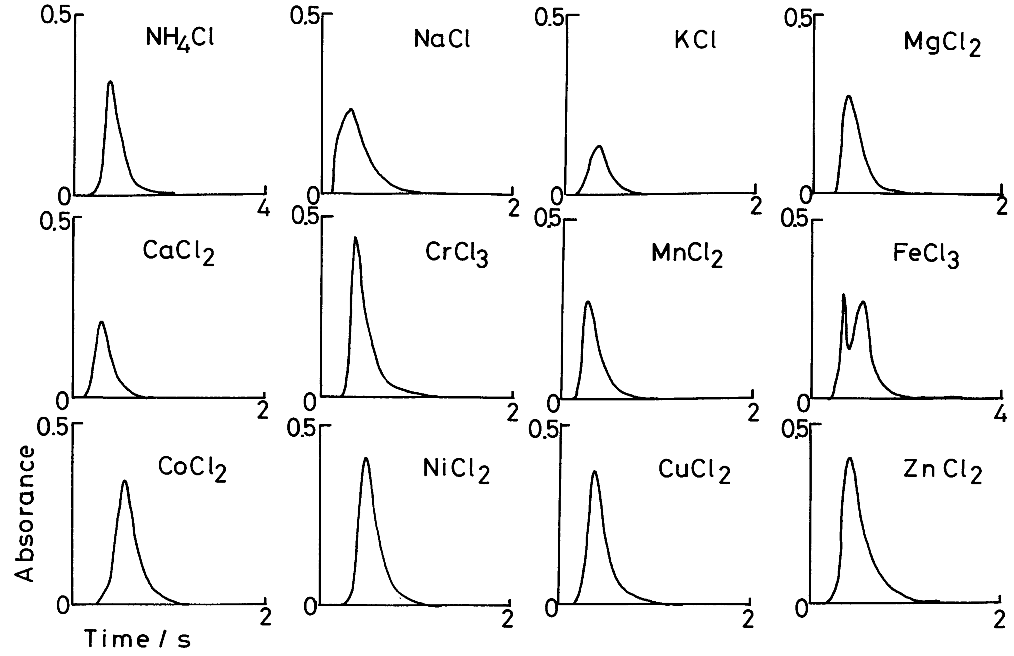


Fig. 1. Atomic absorption signals for lead in various chloride matrices. Analyte; Pb 1 ng with 20 μg of cation, atomization temperature; 3270 K (normal heating) for iron chloride and ammomium chloride matrices and 2700 K (maximum heating) for others, tube; NPG.

iron). The spectral line and slit width were 283.3 and 1.3 nm for Pb and 248.3 and 1.3 nm for Fe, respectively.

A stock solution (1 mol l^{-1} HNO_3 soln), 1000 mg kg^{-1} for the Pb used, was a commercially available standard solution (Wako Pure Chemical Industry, Ltd.). An aliquot of this solution was diluted with water to a suitable concentration before use. The iron hydroxide sample which occluded lead was prepared from an aqueous solution of 1000 mg l^{-1} of Fe(III) as its nitrate or chloride containing 100 μg l^{-1} of Pb, using aqueous ammonia. All other reagents were of analytical reagent grade. Distilled water was purified by a Milli-Q system.

Results and Discussion

Atomic Absorption Signals for Lead. The atomic absorption signals for lead were measured in various chloride matrices: ammonium, sodium, potassium, magnesium, calcium, chromium(III), manganese, iron(III), cobalt(II), nickel, copper, and zinc chlorides. The observed signals are shown in Fig. 1. A typical double-peak signal was observed in iron(III) chloride, where the initial and latter peaks referred to the first and second peaks, respectively. In cobalt(II), sodium and potassium chlorides matrices, signals with a shoulder were also observed. In the present study, the mechanism of double-peak formation was studied because iron is an important component in biological materials, steel and so on.

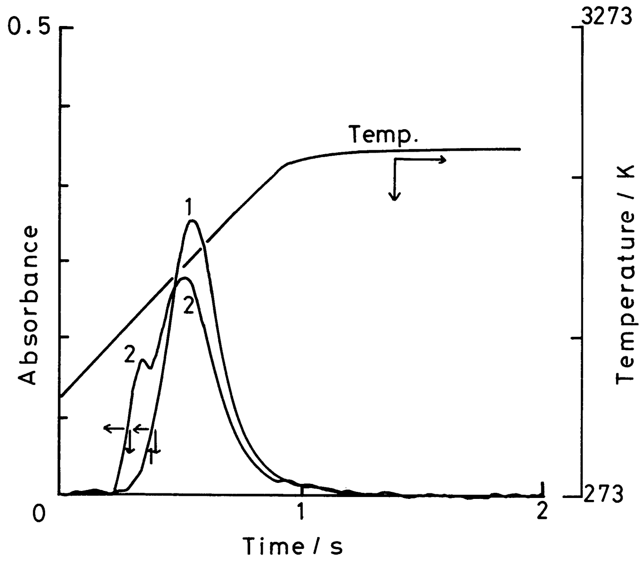


Fig. 2. Atomic absorption signals for lead in iron(III) nitrate (1) and chloride (2) matrices and time-temperature profile. Analyte; Pb 1 ng with 20 μg of Fe, atomization temperature; 2700 K, charring temperature; 800 K, tube: NPG.

Appearance of Double Peaks in the Iron(III) Chloride Matrix. Typical atomic absorption signals for lead in the iron(III) nitrate and chloride matrices are shown in Fig. 2, together with the temperatue profile for the NPG tube. With the chloride ion, a double-peak signal was observed, but not with the nitrate. The appearance temperature (T_{app}) of the signal was 1217±22 K in the iron(III) chloride matrix and 1304±8 K in iron(III) nitrate. Fig. 2 shows that the position of the second peak is in agreement with the position of the peak in iron(III) nitrate.

As shown in Fig. 3, for a PG tube, double peaks (signal 1) were also observed in the iron(III) chloride matrix, but not in the nitrate. The second peak, which is in agreement with the peak in iron(III) nitrate (signal 2), appeared as a shoulder at a heating rate of 1200 K s^{-1} for atomizing, while only the first peak (signal 3) was observed at 362 K s^{-1}. The appearance temperature was 1157±5 K in the iron(III) chloride and 1306±5 K in the iron(III) nitrate. Thus, the chloride matrix atomizes lead at a lower temperature than does the nitrate for both the NPG and PG tubes.

Both the charring temperature and time affected the peak shape of the atomic absorption signal for lead in iron(III) chloride. Fig. 4 shows the effect of the charring temperature on the peak shape, where the

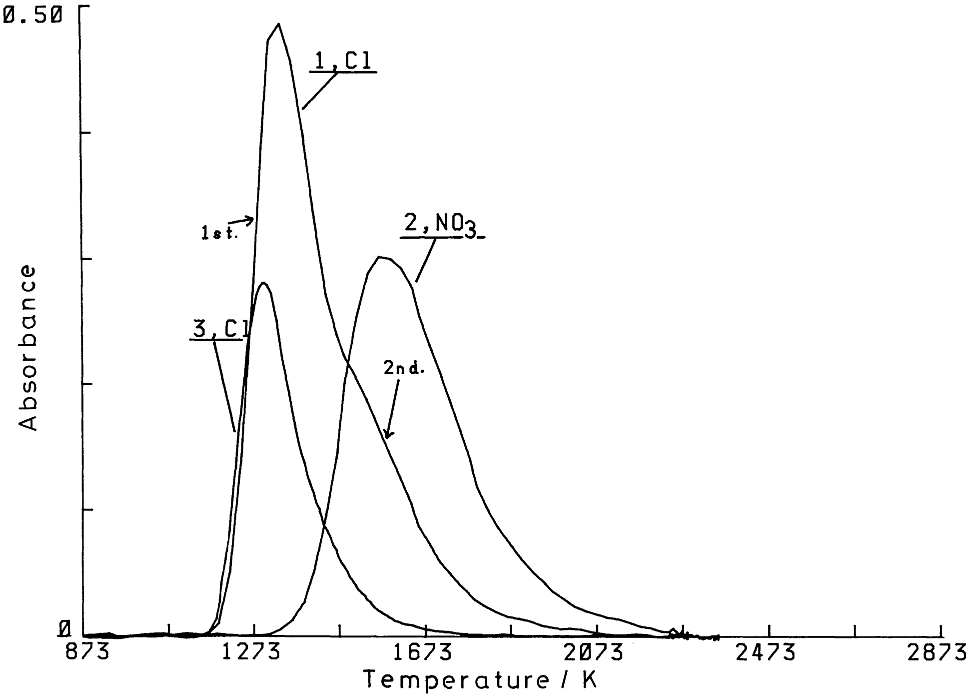


Fig. 3. Atomic absorption signals for lead (Pb: 1 ng) using the PG tube. Charring temperature; 800 K. 1: FeCl$_3$ 0.2 µg of Fe; atomization temperature; 2700 K, 2: Fe(NO$_3$)$_3$ 0.2 µg of Fe; 2700 K, 3: FeCl$_3$ 0.2 µg of Fe, 3000 K.

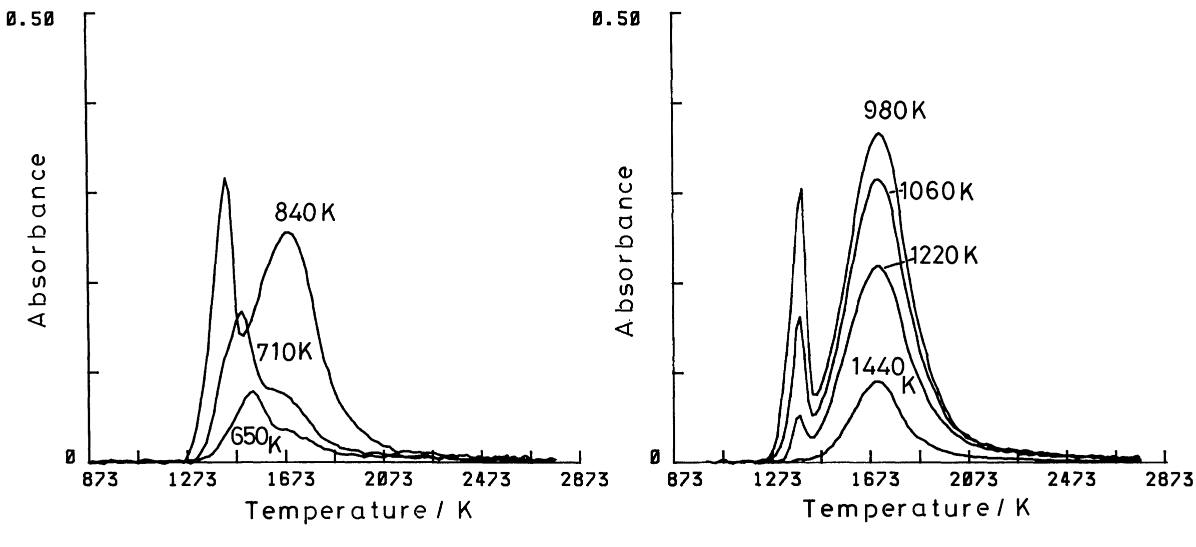


Fig. 4. Effect of the charring temperature on the peak shape. Analyte: Pb 1 ng with 20 µg of Fe(FeCl$_3$), atomization temperature; 3200 K, hold time in charring step; 5 s, tube; NPG.

signals in the range of 650—840 K are indicated in the left-hand figure and those in the range of 980—1440 K in the right-hand figure. Fig. 4 shows that at a charring temperature of 710 K double peaks are clearly observed, while at 1440 K the first peak disappeared and only the second remained. The appearance temperature of the isolated second peak (1308±4 K) is also in agreement with that (1304±8 K) in the iron(III) nitrate matrix. Furthermore, Fig. 5 shows that with a hold time of 5 s in the charring stage (charring temp.: 1060 K), double peaks can be clearly seen. On the other hand, within 20 s the first peak almost disappeared and the second one remained without a change in absorbance. This result suggests that an intermediate compound for the first peak is more volatile than that for the second.

Effect of Iron and Chloride Ions on the Peak Shape. The effects of iron and chloride ions on the atomic absorption signals for lead are shown in Fig. 6; a charring temperature of 800 K was used. The concentrations of iron(III) and chloride ions were controlled with iron(III) nitrate and ammonium chloride, respectively, since both nitrate and ammonium ions scarcely contribute to lead atomic absorption.

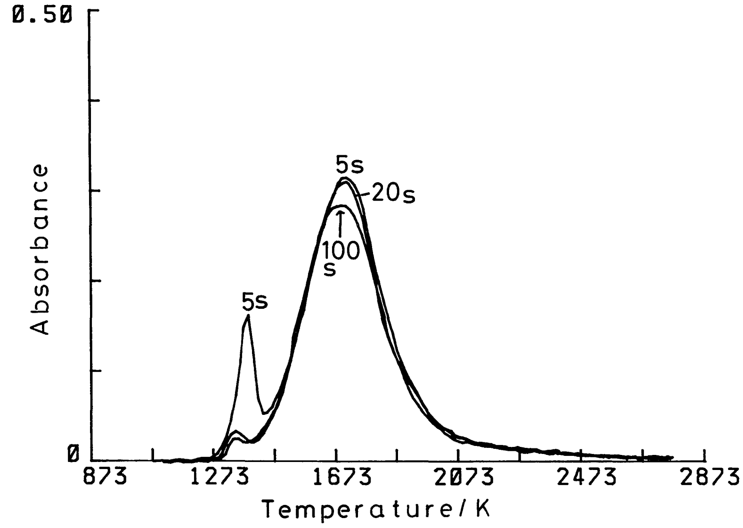


Fig. 5. Effect of the hold time in the charring step on the peak shape. Analyte; Pb 1 ng with 20 µg of $Fe(FeCl_3)$, atomization temperature; 3270 K (normal heating), charring temperature; 1060 K, tube; NPG.

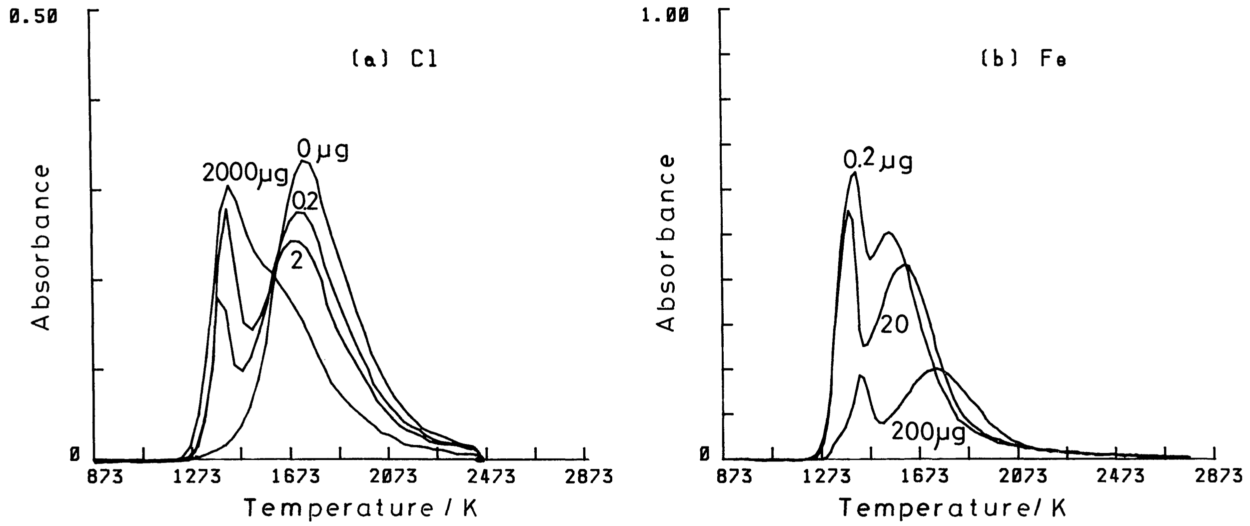


Fig. 6. Dependence of atomic absorption signals for lead on chloride and iron(III) ions added. Charring temperature; 800 K, tube; NPG. (a) Pb, 1 ng; $Fe(NO_3)_3$, 20 µg of Fe; NH_4Cl, varied. (b) Pb 2 ng; NH_4Cl, 20 µg of Cl; $Fe(NO_3)_3$, varied. Atomization temperature: (a) 2700 K (maximum heating); (b) 3270 K (normal heating).

Fig. 6(a) shows that increasing the chloride ion content under a constant amount of iron causes an increase in the first peak height and a decrease in the second peak height, with a 12% decrease of the peak area from 0 to 2000 μgCl and without any shift of the peak temperature. The atomic absorption signal for iron in the matrix is shown in Fig. 7, together with that for lead, showing that lead atomizes at the same temperature as does iron. Fig. 6(b) shows that an increase in the iron content shifts the double peaks to the higher temperature side.

Double Peaks for Another Halide Ions. Fig. 8 shows the atomic absorption signal for 2 ng of lead in the presence of ammonium chloride, ammonium bromide, and ammonium iodide with iron(III) nitrate. Double-peak signals were observed in the presence of ammonium bromide and iodide as well as chloride. The values of T_{app} for the first peak are given in Table 1. The T_{app} value is higher in the following order: Cl^- (1214±26 K)<Br^- (1268±11 K)<I^- (1284±10 K).

Recently, Holcombe[9] discussed the use of Ahrrenius-type plots employing the leading edge of the absorbance signal using data from computer simulations; they concluded that the extraction energetics of the gas-phase dissociation processes are likely to be in error. However, in practice, such a method has been applied extensively to the elucidation of the atomization process and has provided valuable information. In the present work we therefore tried to use a similar method. If the intermediate compound leading to the formation of lead halide is responsible for the first peak, the E_a value should be influenced by the variety of halogen. A kinetic analysis of the first peak was carried out by using a correction method;[10,11] the obtained E_a values are also given in Table 1. The E_a values for chloride, bromide, and iodide were 290±17, 258±5, and 252±11 kJ mol^{-1}, respectively. The E_a value decreases in the order $Cl^- > Br^- \geqq I^-$. The tendency for the decrease of E_a is in agreement with that for the bond energy: 316±29 for PbCl(g), 262±38 for PbBr(g), and 213±38 for PbI(g) in kJ mol^{-1} at 1250 K.[12]

Therefore, the above results are, at least, compatible with the inference drawn here: the first peak may be caused by the dissociation of lead halide.

Effect of Iron on Appearance of the First Peak.

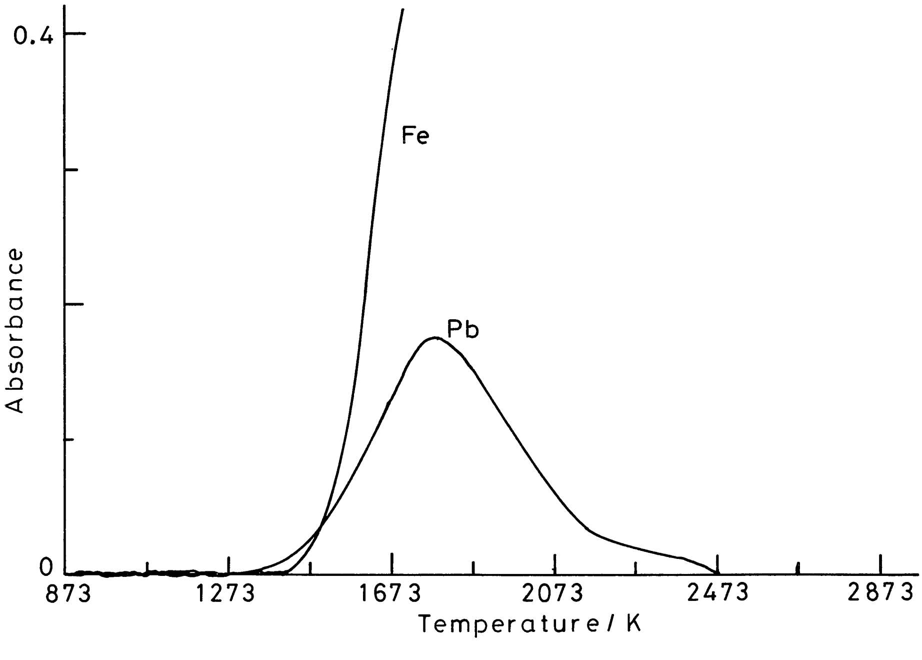


Fig. 7. Atomic absorption signal profiles for lead and iron. Pb: 1 ng; $Fe(NO_3)_3$, 20 μg of Fe. Atomization temperature; 3270 K (maximum heating), charring temperature; 800 K, tube; NPG.

Table 1. Signal Appearance Temperature (T_{app}) and Activation Energy (E_a) for the First Peak

Halogen[a)]	T_{app}/K	E_a/kJ mol^{-1}	Bond energy[b)] at 1250 K/kJ mol^{-1}
Cl	1214±26	290±17	316±29 Pb–Cl
Br	1268±11	258±5	262±38 Pb–Br
I	1284±10	252±11	252±11 Pb–I

a) 2 ngPb with 20 μgCl, 45 μgBr, or 72 μgI as ammonium salt, and 20 μgFe as nitrate. b) Data from Ref. 12.

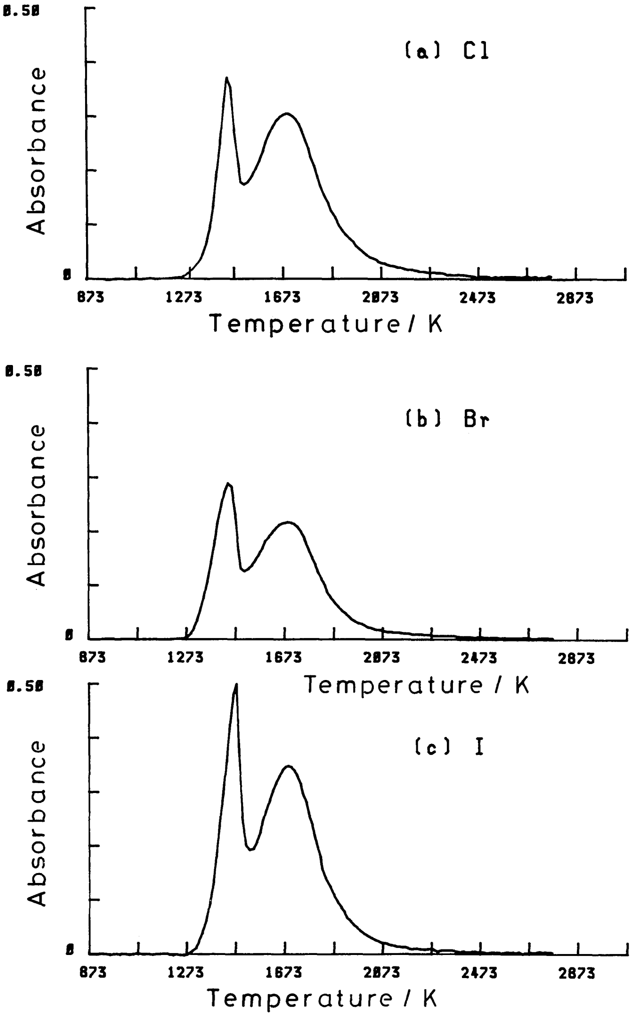


Fig. 8. Atomic absorption signal for lead (Pb: 2 ng) in a matrix of iron(III) nitrate and ammonium halide. (a) $Fe(NO_3)_3$, 20 µg of Fe; NH_4Cl, 20 µg of Cl. (b) $Fe(NO_3)_3$, 20 µg of Fe; NH_4Br, 45 µg of Br. (c) $Fe(NO_3)_3$, 20 µg of Fe; NH_4I, 72 µg of I. Atomization temperature; 3270 K (normal heating), charring temperature; 800 K, tube: NPG.

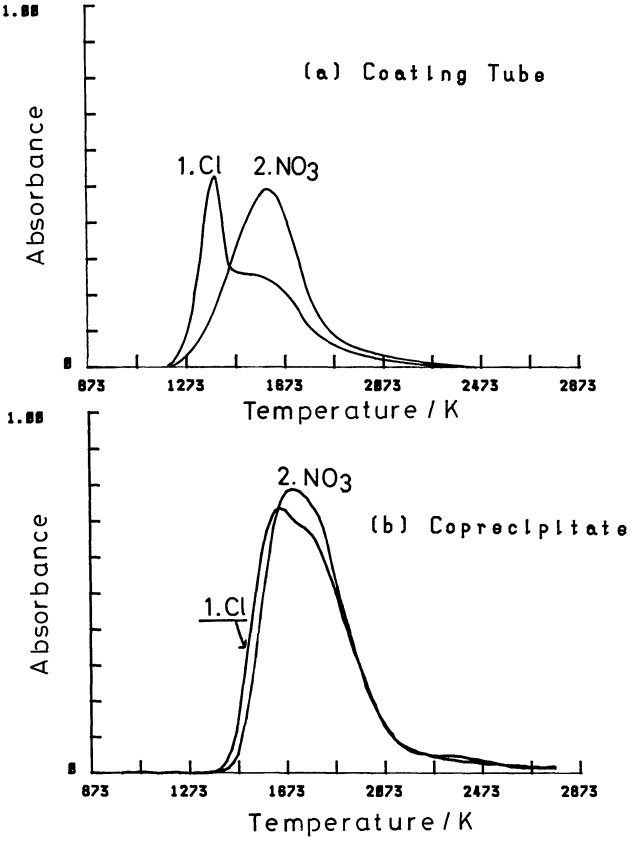


Fig. 9. Comparison between atomic absorption signals for lead. Atomization temperature: 3270 K (normal heating). Charring temperature: 800 K. (a) 1: Pb 3 ng; NH_4Cl, 20 µg of Cl; 2: Pb 1 ng, tube; NPG coated with iron oxide. (b) Lead in the coprecipitate with iron(III) hydroxide from iron(III) chloride (1) and iron(III) nitrate (2) using aqueous ammonia, tube; NPG.

Wendl and Müller-Vogt[2] reported that some lead chloride was hydrolyzed to PbO, and that the others were removed as PbCl vapor at temperatures greater than 700 K. In this work, however, a reduction of the first peak which resulted from lead chloride was not observed until 900 K in the iron(III) chloride matrix. Frech and Cedergren[3] examined the interference mechanism of iron with the chloride ion and concluded that the formation of volatile lead chlorides, $PbCl_2$ and PbCl, in the gas phase resulted in a reduction of the signal of lead in steel, where high-temperature equilibrium calculations were made under the assumption that $FeCl_2$ and $FeCl_3$ were in the gas, liquid, and solid phases and that Fe_2O_4, Fe_3O_4, FeO, and Fe were in the solid phase. In the present work, as mentioned in Fig. 6(b), an increase of the iron content shifted both peaks in the double-peak signal to a higher temperature, indicating that iron also affected the atomic vapor formation of lead.

Iron hydroxide, oxide, and chloride are produced in the drying stage from an iron(III) chloride aqueous solution; the hydroxide changes to the oxide during the charring stage by a reaction with either oxygen or water. At first, in order to investigate the effect of iron oxide on the atomic absorption signal for lead, measurements were performed for two types of solution samples with and without ammonium chloride, using an NPG tube coated with iron oxide. The result is shown in Fig. 9(a). The figure shows that a double-peak signal is observed for lead with the ammonium chloride solution, while a single-peak signal is observed for lead without ammonium chloride. The E_a and T_{app} values (294±15 kJ mol^{-1} and 1214±26 K) for the first peak in the ammonium chloride matrix are in agreement with those values (290±17 kJ mol^{-1} and 1217±22 K) for the first peak in the iron(III) chloride matrix within experimental error. These agreements of the E_a and T_{app} values show that the first peak in the ammonium chloride matrix is due to the same mechanism as the first peak in the iron(III) chloride matrix. In the second, in order to investigate the effect of iron hydroxide, measurements were performed for lead coprecipitated with iron hydroxide from either iron(III) chloride or iron(III) nitrate solutions. The result is shows in Fig. 9(b). The atomic absorption signals are not in agreement with the first peak mentioned above. These results, thus, indicate that iron oxide formed on the charring stage inhibits vaporization of lead chlorides, leading to the appearance of only the first peak.

In conclusion, atomic absorption signals with double peaks were observed for lead in an iron(III) chloride matrix and the chloride ion was responsible for the appearance of the first peak resulting from thermal dissociation of lead chloride. The iron was also responsible for shifting each peak to a higher temperature; the iron oxide formed during charring inhibited the charring loss of lead chloride.

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