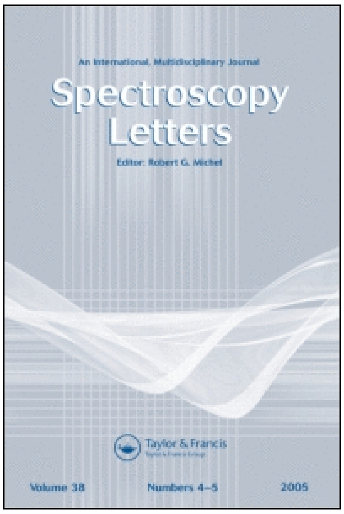

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Metal Speciation by Atomic Absorption Spectroscopy. The Two Stage Atomizer

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To cite this Article Robinson, J. W. and Jowett, P. L. H.(1983) 'Metal Speciation by Atomic Absorption Spectroscopy. The Two Stage Atomizer', Spectroscopy Letters, 16: 3, 159 — 179
To link to this Article: DOI: 10.1080/00387018308062332
URL: http://dx.doi.org/10.1080/00387018308062332

SPECTROSCOPY LETTERS, 16(3), 159-179 (1983)

METAL SPECIATION BY ATOMIC ABSORPTION SPECTROSCOPY. THE TWO STAGE ATOMIZER

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A. INTRODUCTION

Thermal analysis (T.G.A., DTA, etc.) has been extensively used for speciation analysis. However, it is relatively insensitive temperature limited, and has not been useful at the trace level.

In contrast, atomic absorption spectroscopy is a very sensitive technique capable of detecting low concentrations of metals. The chemical form of metal components affects the atomization process and is the cause of chemical interferences. In practice, chemical interferences are reduced by rigidly controlling the heating programs used in carbon atomization. Studies have been made to understand the interference mechanisms and reduce them. Attempts to use atomic absorption and emission for metal speciation have been published.[1-17] However, to date, all systems have been single stage, i.e. vaporization and atomization took place in the same section of the instrument.

A two-stage atomizer was first reported by Robinson and Rhodes.[18] The results of a preliminary study in its use in speciation analysis are reported here. The system consisted of two molybdenum sections, an atomization section and a vaporization section, which were heated separately. The sample was volatilized at varying temperatures in the vaporization section and the vapors were swept into the atomization section which was kept at 2200°C. Atoms were formed in the atomization section and swept into the optical light path, where absorption took place. Even when vaporization took place at low

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temperatures, the sample was atomized by the high temperature atomizer and absorption signals were recorded. The results that were obtained were correlated to those observed using a slightly modified commercial atomic absorption unit.

B. EXPERIMENTAL

1. Chemicals

The inorganic salts that were used were commercially available reagent grade. For soluble salts, standard aqueous solutions were prepared with distilled deionized water. For insoluble salts, a saturated solution was used; if necessary, a suspension was utilized.

2. Equipment

a. Perkin Elmer 403-HGA 2000

A commercial PE graphite furnace was modified to produce a slow heating ramp. A switch was placed in parallel to the HGA atomizing temperature adjustment button. It was turned to the "on" position while the adjusting potentiometer was slowly turned with a kymograph.

Nitrogen was used as the purge gas and was introduced at the furnace windows. The flow rate was adjusted to 180 cc/min to obtain the best compromise between peak height and peak width while using a heating ramp of 7.5°/min over a temperature range of 100-2000°C.

The samples were delivered with a 10 μL Hamilton syringe.

b. Two-Stage Atomizer

i. Interior Components. A diagram of the molybdenum analyzing sections, the carbon supports and the center electrode is depicted in Figure 1. The thermocouple used to monitor the temperature of the vaporization section was placed just above it, as shown in the diagram.

Each molybdenum piece was connected to the center carbon electrode, and to the end carbon supports. These in turn made electrical connections with their respective water cooled brass electrodes. The center carbon piece was held in position by two water cooled brass electrodes.

Vaporization tube: 15/64" id, 1/4" od, 1" long. Atomization tube: 5/16" id, 3/8" od, 3/4" long leading to a section 1/4" od. The optical light path was drilled through this piece. See Figure 1.

It was found that the distance between the molybdenum pieces was critical. A convenient distance of 1/8" - 1/4" was used.

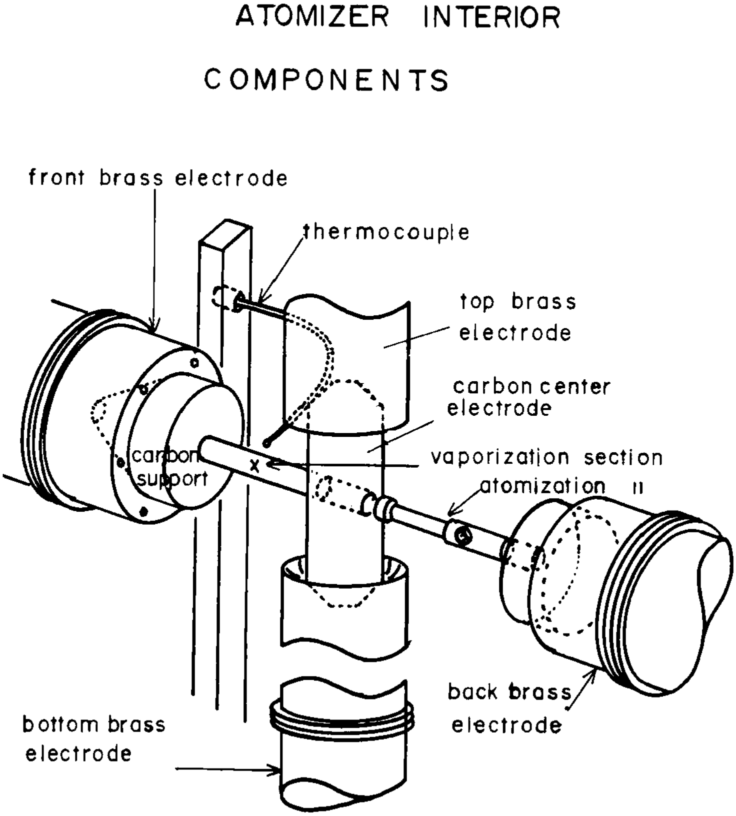


Figure 1.
The four brass electrodes were designed to accomodate a large electrical connection area. They are also water cooled. The thermocouple monitored the temperature of the vaporization section.

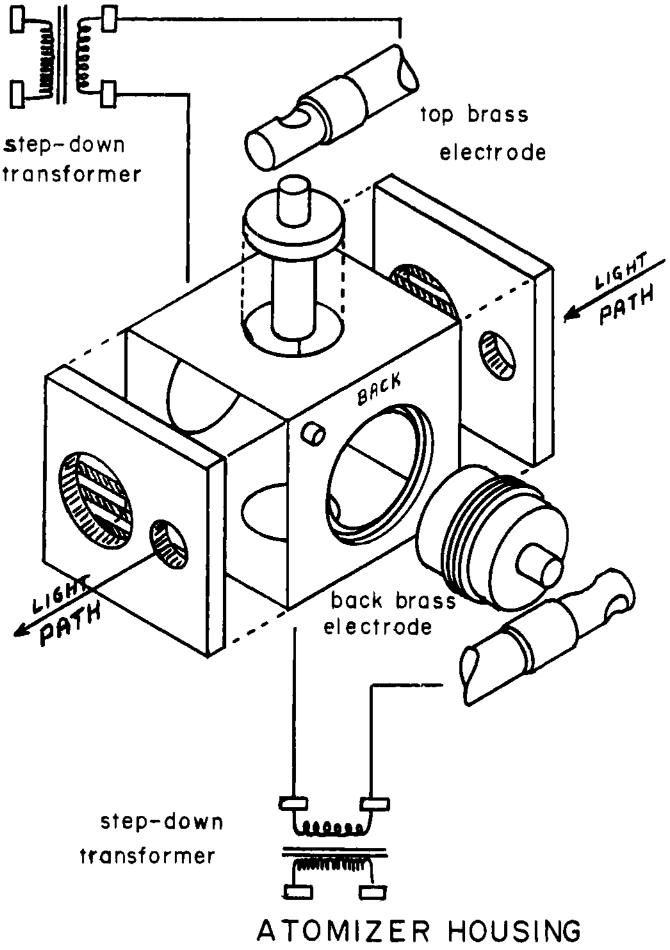


Figure 2
Exploded view of the atomizer housing showing the removable doors, top and back brass electrodes, and viewing windows.

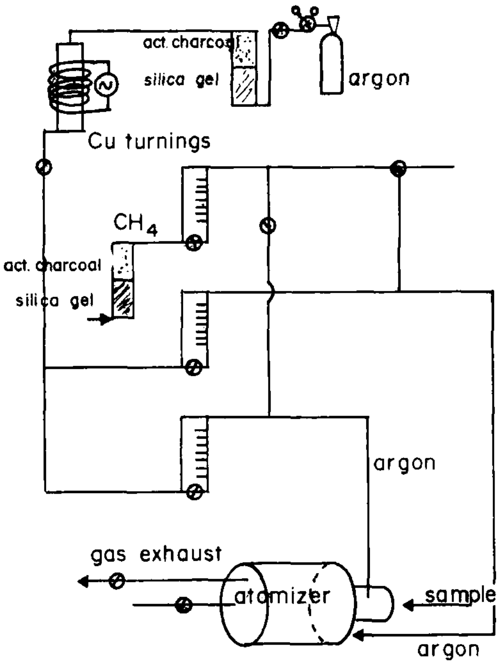


Figure 3
Diagram of the gas system for the two-stage atomizer. Argon was used to provide an inert atmosphere. It was dried with silica gel. Trace components were removed with activated charcoal. Oxygen was removed with hot copper turnings. Separate streams entered the atomizer. Cleaned methane was only mixed with the argon going into the atomizer body.

The chromel-alumel thermocouple was calibrated with an optical pyrometer (Leeds and Northrup model 9632-C, 775°-2800°C) to measure temperatures of the vaporization tube above 1000°C. Below 1000°C, the molybdenum section temperature was calibrated by placing another chromel-alumel thermocouple within the tube.

ii. Atomizer Housing. A water cooled housing for the atomizer is depicted in Figure 2. The housing had two removeable water-cooled doors, each including a viewing window and the optical light path window.

The housing also provided ports for gas inlet and exhaust and for two thermocouples.

iii. Gases. The system of gases that was used is depicted in Figure 3.

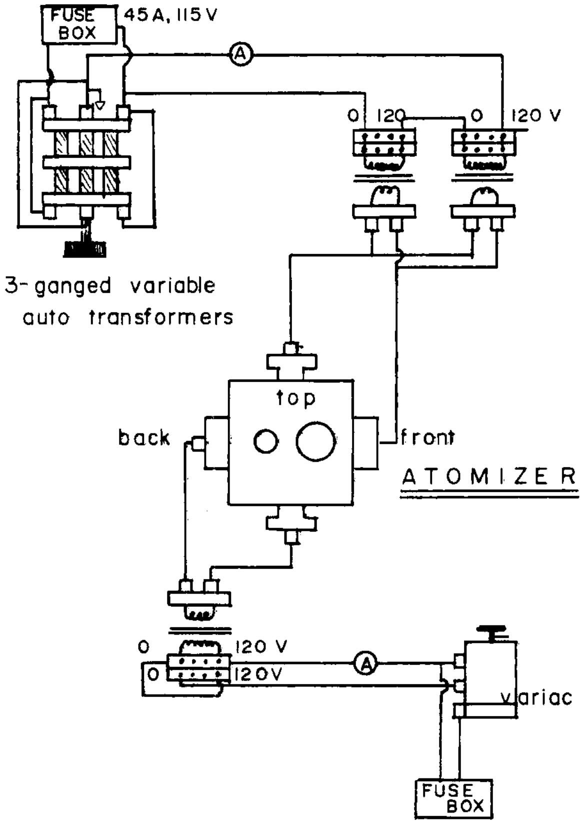


Figure 4
Electrical diagram of the two-stage atomizer. The variable auto-transformers were used to gradually heat the vaporization section. The variac shown at the bottom of the figure was used to control the current provided to heat the atomization section. In neither case were the full line voltages reached in normal operations.

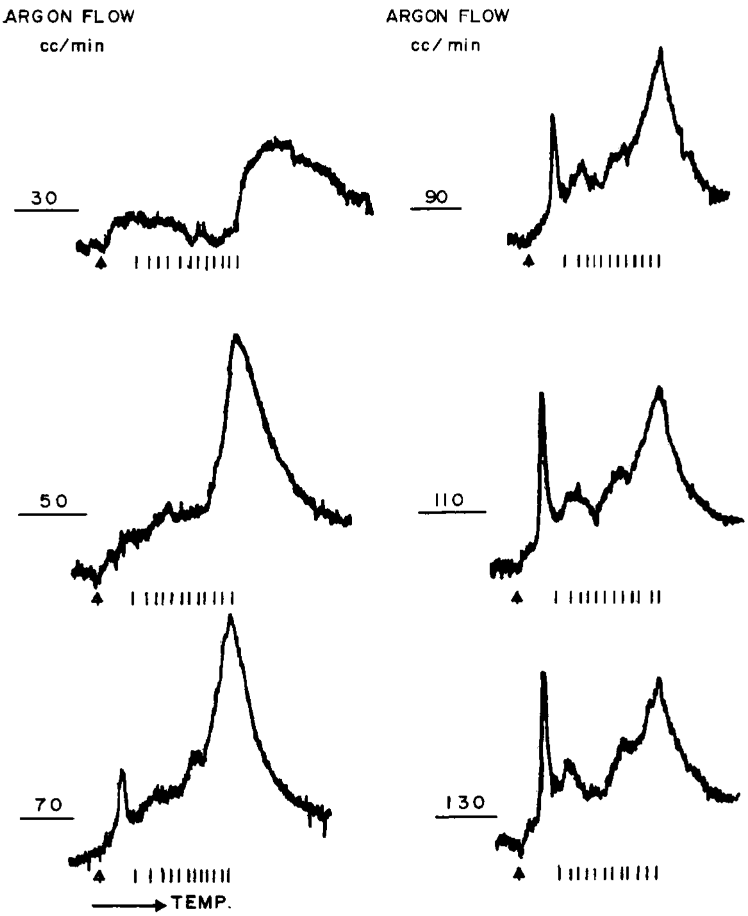


Figure 5
Effect of the carrier gas flow rate on the thermal-absorption signal of 100 ppm lead chloride, using the two-stage atomizer. At increased flow rates better resolution and fine structure were observed.

Argon was used as the inert atomizer gas. It was dried, cleaned and scrubbed of oxygen by passing it through silica gel, activated charcoal and heated copper turnings, respectively. The argon flow into the atomizer body (250-750 cc/min) was separately controlled from that going through the analyzing tubes (10-230 cc/min).

Methane was used to remove free oxygen for the system. It was mixed only with the argon going into the atomizer body (5-10 cc/min). It was dried and cleaned in the same fashion as the argon.

Helium was used as the filler gas for the demountable hollow cathode.

iv. Electrical System. The atomization section power was regulated with a 18A, 115V variac. The line voltage was stepped down with a Signal Transformer (9V, 500A).

The vaporization section power was regulated with two 20A ganged variacs. Two step down transformers were used (12V, 500A) in series. A diagram of the system is shown in Figure 4.

v. Optical and Signal Processing Systems.

- a. Demountable hollow cathode lamp, designed and built in our own laboratories.
- b. Mechanical chopper fitted with a reed switch for phase locking.
- c. Jarrel-Ashe 0.5 m monochromator; 1180 lines/mm grating and R-106 photomultiplier.
- d. GCA-McPherson/Heath Photometric read out amplifier, model EU 703-31.
- e. Beckman 10" strip chart recorder.

vi. Precision sampling. 10 μL syringe, with a removeable 4" needle.

c. Air Sampling

- i. Dyna-Vac diaphragm pump, model 4 K Cole Palmer Instruments.
- ii. Gelman glass fiber filters, type A, no 61694.
- iii. Dwyer flow meter, 0-5 l/min.

C. PROCEDURE

1. Two-Stage Atomizer

a. Flow Rate of Argon

Argon was used to sweep the evolved gas from the vaporization section to the atomization section. Figure 5 shows the effect of the carrier gas flow rate on the absorption signal for lead chloride (100 ppm). Based on the results, a flow rate of 110 cc/min was normally used.

b. Heating Rate

Because the heating rate was manually controlled it was not **very** linear. The heating time of a cycle was therefore used for comparison purposes. Figure 6 shows the results of changing the heating time. Based on the results, a heating cycle of 5.5 min was used since this gave adequate resolution.

c. Vaporization Section Temperature-Depth Profile

For good reproducibility, it was important to place the sample in the hottest portion of the vaporization tube. This was necessary because there was a marked temperature gradient along the tube.

d. Sample Introduction

A 4" needle was used to introduce the sample. A smearing problem occured if the syringe was not held, and withdrawn steadily and concentrically because a slight syringe movement caused a large needle tip travel. This problem was alleviated by using an injector support.

2. Air Sampling

a. Sample Collection

Ambient air (14-30 m^3) was drawn through a 1" diam. Gelman 0.3 filter at a rate of 3-5 l/min. Sample discs (1/4") were punched from around the center of the filter. The argon/methane mixture entering the atomizer housing was temporarily stopped while introducing the filter discs into the vaporization section.

D. RESULTS AND DISCUSSION

1. Standards and Solutions

a. Two-Stage Atomizer

i. Lead. Several lead compounds were analyzed and the results obtained with the two-stage atomizer for acetate, nitrate, and oxide are depicted in Figure 7. The oxide exhibited only one prominent peak which was at 1500°C. The nitrate and acetate also showed a single peak at 1500°C. The latter are reported to decompose to the oxide at 400°C. Consequently, the observed absorption traces were probably that of the oxide. Solutions of lead carbonate and molybdate were also analyzed and the recorded absorption traces

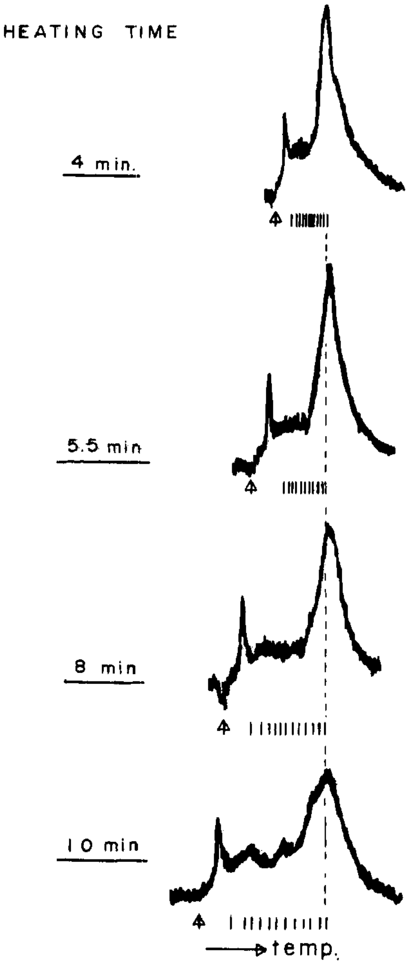


Figure 6
Effect of the heating rate on the thermal-absorption signal for 100 ppm lead chloride. The 5.5 minute cycle was preferred because the signals were sufficiently sharp and the heating time was short.

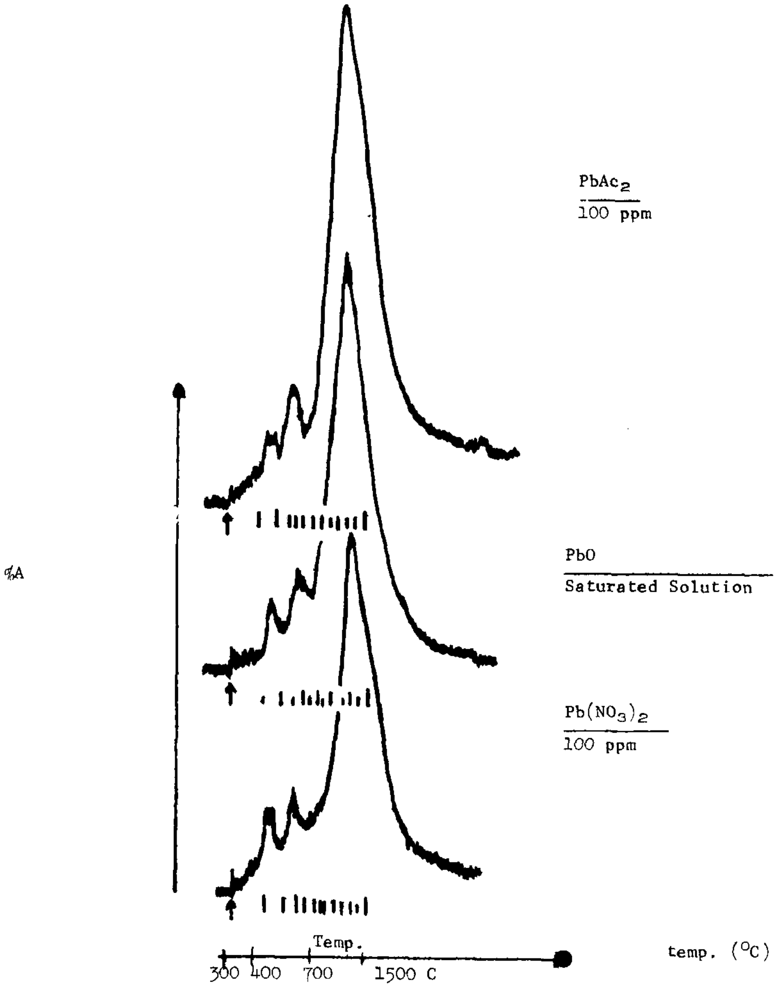


Figure 7
Thermal-absorption curves of lead acetate, oxide and nitrate using the two-stage atomizer. The low temperature decomposition of the oxyanions produced absorption traces similar to that of lead oxide.

coincided with that of the oxide. These salts also decompose to the oxide at low temperatures.

The lead chloride exhibited a sharp signal at 310°C as shown in Figure 8. The signal was believed to be due to the volatilization and atomization of the halide. The signal at 1500°C was probably due to the oxide.

When in solution, the metal would be ionic and hydrated. Upon drying, these ionic samples may produce large amounts of the oxide and some $PbCl_2$. The absorption traces may be an indication of the distribution of the lead between these forms after drying from solution.

Similar results to the chloride were observed with lead iodide. Figure 8 shows the absorption traces that was obtained using a saturated solution of the iodide. Depicted are the two signals observed at 330°C and 1600°C. As in the case of the chloride, the signal observed at 330°C was believed to be due to the halide species, and that occuring at 1600°C to the oxide.

Figure 8 also shows the absorption trace of a lead sulphate. The results showed the appearance of two prominent signals occuring at 680°C and 1450°C.

ii. <u>Cadmium.</u> The absorption traces that were recorded for cadmium acetate, nitrate, and oxide are represented in Figure 9. The oxide exhibited a simgle peak at 700°C which was considerably lower than the reported sublimation of the amorphous form of the salt. The small sample size and the considerable carrier gas flow rates passing over the sample were thought to be an important factor contributing to the large temperature difference.

The cadmium acetate and nitrate appeared at similar temperatures as the oxide, namely, 600°C and 700°C, respectively. This suggested that decomposition to the oxide occured below these temperatures, confirmed by TGA studies.

The absorption traces of cadmium chloride and iodide revealed the presence of two prominent signals occuring at 340° and 650°C, in each case (see Figure 10). Analogous to the lead halides, it is believed that the lower temperature signals were due to the halide species. Those occuring at 650°C were thought to be due to the formation of oxide as a result of heating hydrated ions produced during dissolution.

The analysis of some zinc compounds was also attemped using the two-stage atomizer, but considerable lack of reproducibility was encountered. This problem

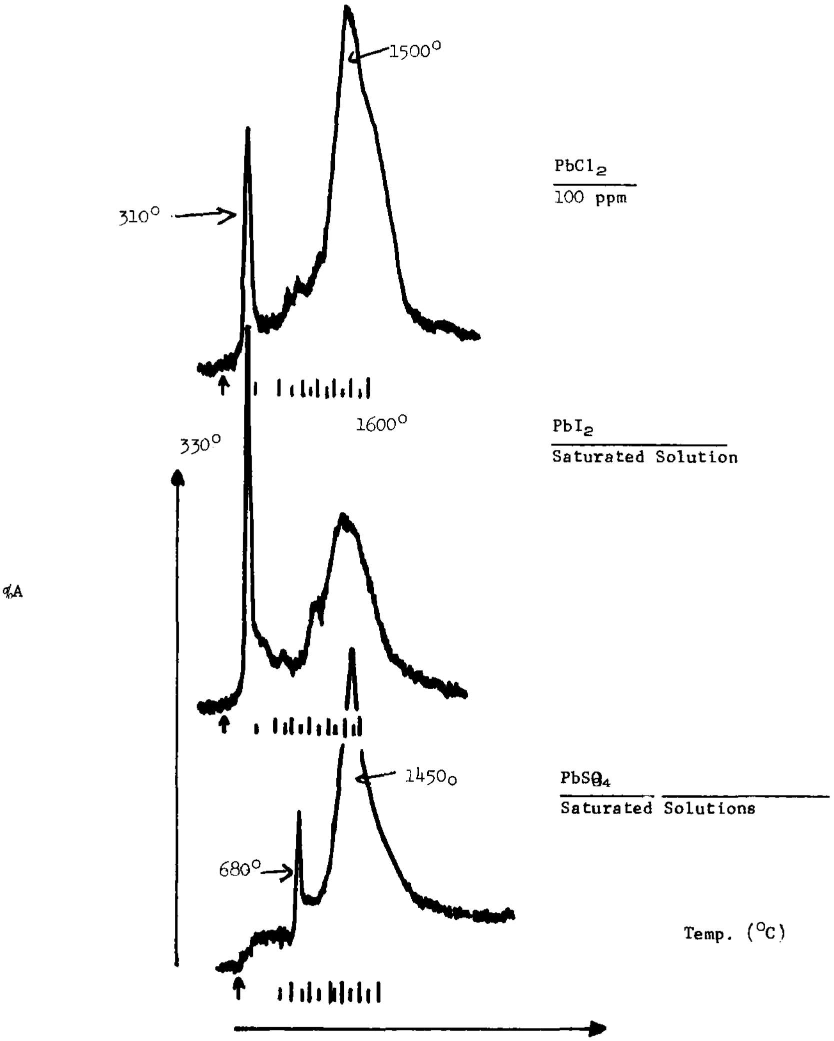


Figure 8
Thermal-absorption curves obtained with the two-stage atomizer for lead chloride, iodide and sulfate. Each exhibited unique low temperature peaks, as well as at higher temperatures (1500°, 1600° and 1450°, respectively) which were thought to correspond to the oxide.

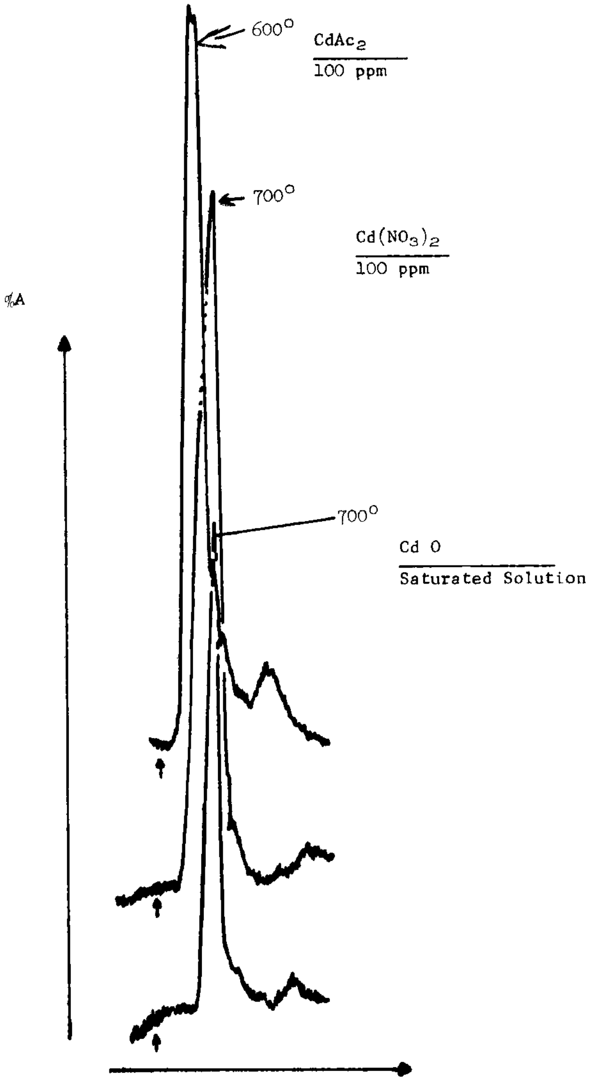


Figure 9
Results obtained using the two-stage atomizer for cadmium acetate, nitrate and oxide. Essentially no differences were observed between these compounds within experimental error, due to the low temperature decompostion of the oxyanions.

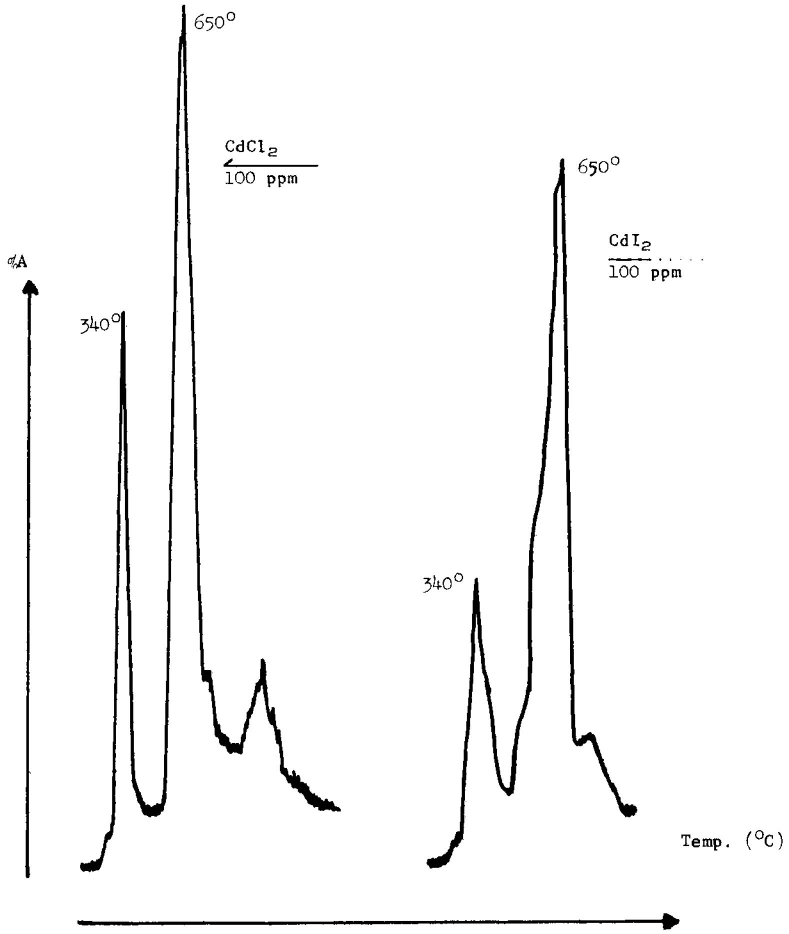


Figure 10
Results obtained for cadmium chloride and iodide using the two-stage atomizer. These compounds exhibited a low temperature signal (340°) which was thought to be the halide species. The signals observed at 650° were believed to be due to oxide, formed when heating the sample solutions.

was thought to be due to contamination offurnace for this highly sensitive element. Mercury compounds were also examined, but because of their high volatilities at low temperatures of the vaporization section, we were unable successfully to observe the thermal degradation characteristics.

b. Results Using the PE Graphite Furnace

i. Lead. Figure 11 shows the results obtained for lead chloride, iodide, nitrate, oxide, and sulfate using the PE graphite furnace. In contrast to the absorption trace observed using the two-stage atomizer, lead chloride exhibited only one signal using the PE furnace. It was observed at 1130°C and coincided with the signal observed for the lead oxide. The reduced temperature compared to the two-stage atomizer was probably due to the reducing power of the carbon process. The low temperature signal due to the volatilization of the lead chloride was not observed. This shortcoming was probably due to the inability of the PE furnace to atomize the evolved gases at the low temperatures. Likewise, the absorption curve of the lead iodide revealed only one signal, observed at 1180°C.

The thermal-absorption traces recorded for the lead nitrate, oxide and sulfate also exhibited a single peak in each case. The respective signals were observed to occur at 950°, 990° and 1010°C. These variations observed in these temperatures were thought to be mostly due to the conditions of the graphite tube. They reflected a lowering of the observed temperatures as a function of the furnace firing number.

ii. Cadmium. The signals obtained with the cadmium chloride and iodide, acetate, nitrate, and oxide are depicted in Figure 12. The signals observed at 340°C for the chloride and iodide using the two-stage atomizer were not detected using the PE graphite furnace. Reflecting the inability of these types of furnaces to atomize at low temperatures, the large signals observed at 850°and 830° for the chloride and iodide, respectively, coincided within experimental error, with the signal obtained for the cadmium oxide.

The peak that was observed for cadmium oxide occured at 800°C. Those for actate and nitrate were observed at 830° and 760°C, respectively. These are thought to be due to the oxide since the compounds decompose at low temperatures. The temperature variations that were observed were presumably primarily due to the age of the graphite furnace.

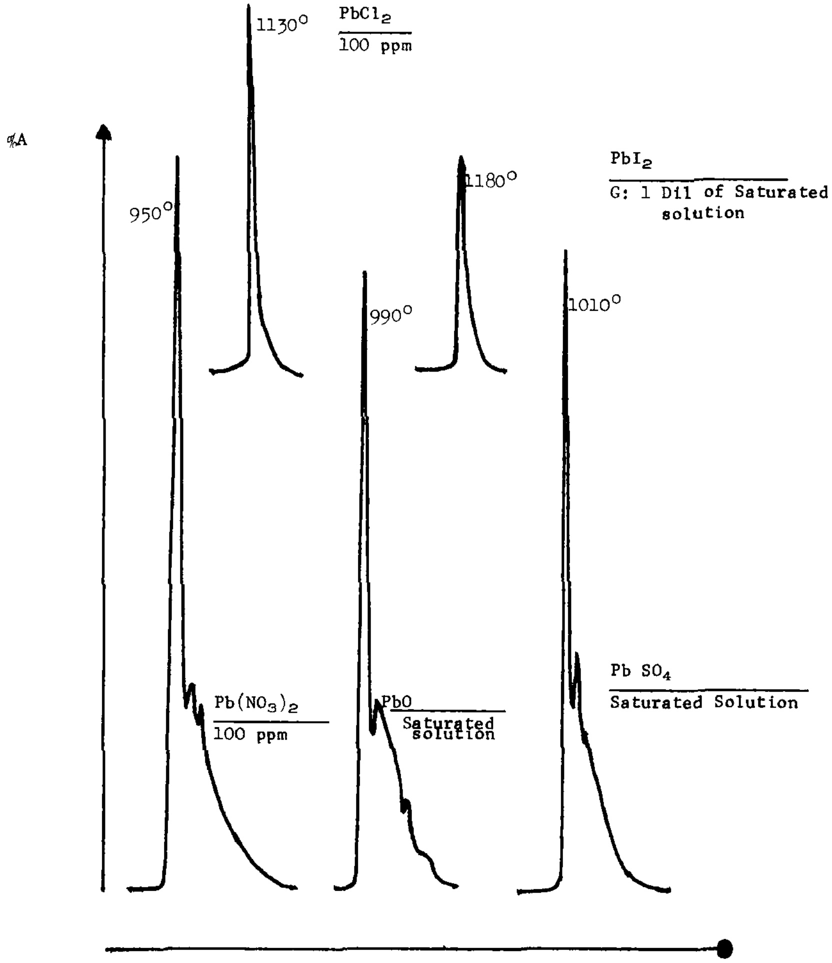


Figure 11
Absorption traces of lead compounds using the PE graphite furnace system. Depicted are lead chloride, iodide, nitrate, oxide, and sulfate. Each compound exhibited only one signal at about the same temperature, within experimental error (tube age especially). This suggested that the oxide species was being observed but the low temperature halide volatilization escaped detection.

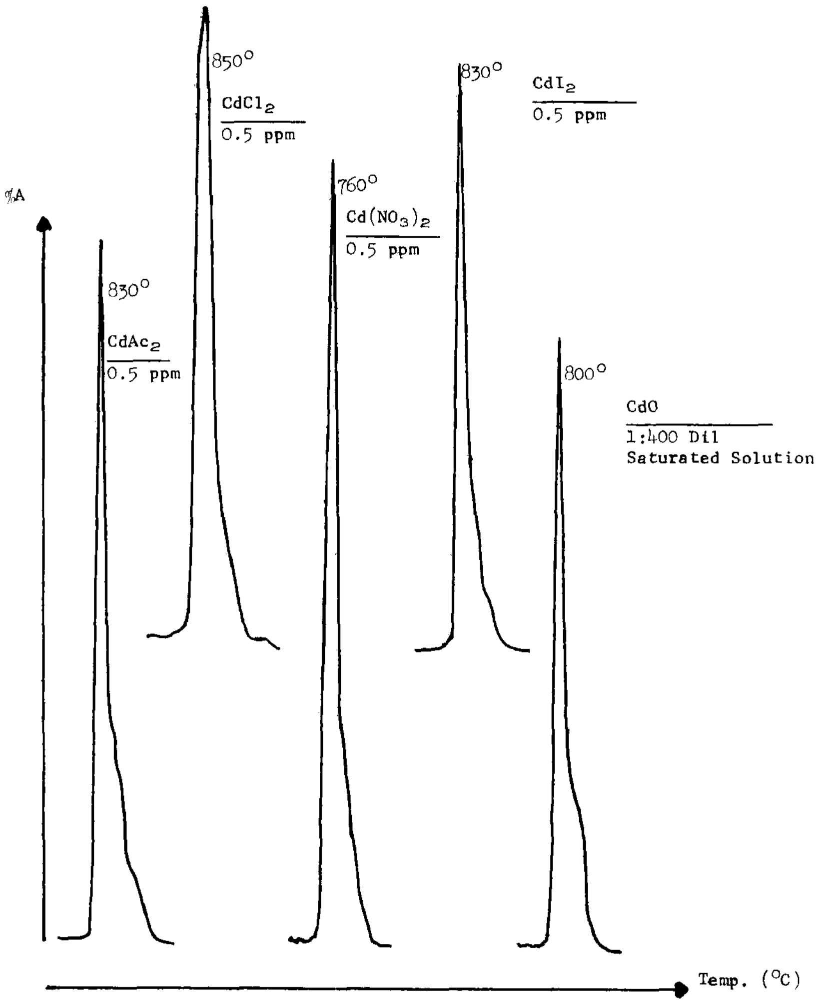
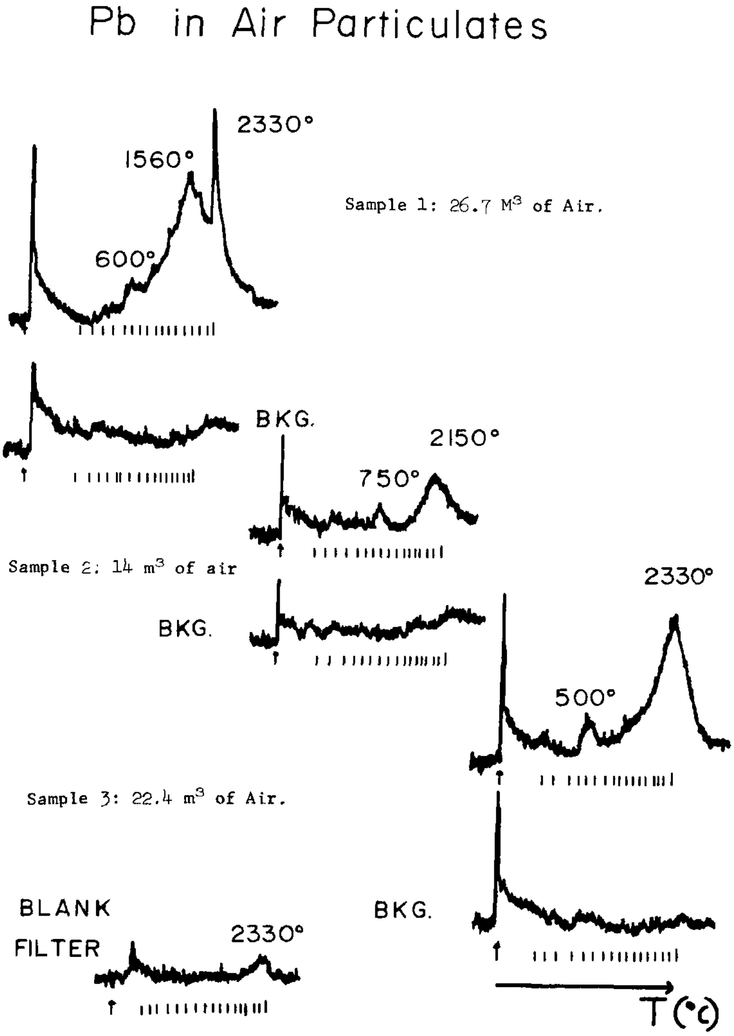


Figure 12

Results recordes for various cadmium salts using the PE graphite system. All compounds exhibited only one signal which were essentially the same within experimental error. This suggested that the oxide was being detected in each case, and that low temperature volatilization of the halides, which was seen with the two-stage atomizer, escaped detection



Sample 1: 26.7 M^3 of Air.

Sample 2: 14 m^3 of air

Sample 3: 22.4 m^3 of Air.

Figure 13
Thermal absorption traces for three different samples showing the absorption at the 283.3 nm line of lead and D_2 background, for each. The signal at 1560°C was thought to possibly be due to lead oxide. Those at 2330°C and 2150°C was not identified.

2. Lead in Air Pollutants

Lead in air particulates was examined and Figure 13 shows the results obtained for three different samples.

The first sample exhibited a prominent signal occuring at 1560°C which was similar to the lead oxide. It may have originated from one or more lead compounds that decomposed to oxide. The source of the peaks at 2330° and 2150° were not identified. However, it was clear that the technique was sensitive enough for speciation studies at trace levels.

E. GENERAL DISCUSSION

1. Advantages of the Two-Stage Atomizer

The most prominent virtue of the two-stage atomizer system was its ability to monitor continuously for metallic constituents of a sample that was gradually being heated. As a result, volatile species which evolved from the sample at low temperatures could be observed. This effect was clearly observed with the metal halides. The lead sulfate exhibited a similar thermal degradation characteristics.

In contrast, commercial systems did not have this capability because of their furnace design. The latter were designed to eliminate such signals by using a rapid heating ramp to converge the signals. The compounds that are volatilized at low temperatures were not atomized, and therefore not detected.

Secondly, sensitivities are much better than thermal analyzers (TGA). Further studies should provide refinements in qualitative and quantitative applications.

F. CONCLUSIONS

The most favorable attribute of the two-stage atomizer was its ability to detect volatile metal compounds which evolve at low temperatures.

These compounds were not observed with the commercial AAS system because the volatilization occured at temperatures that were too low for atomization to take place.

The sensitivities achieved with atomic absorption were several orders of magnitude better than those using TGA. Sample sizes that are required for the thermogravimetric analyses are in the order of milligrams and are considerably larger than those used with atomic absorption. Thus, the two-stage atomizer has a distinct analytical advantage over TGA in this respect, in addition to its speciation capabilities.

The results obtained with the two-stage atomizer indicated the formation of oxides from dried solutions, probably resulting from hydration of the ion in solutions followed by oxide formation on drying. Consequently, using solutions posed limitations not encountered with solid solutions. Because of the high sensitivity of atomic absorption, it was difficult to load solid standards. The sample sizes were necessarily less than 1 μg in size. Handling and measuring was difficult.

Other applications which will be examined include metal corrosion production and environmental pollution samples.

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