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THE DETERMINATION OF LEAD BY ELECTROTHERMAL  
ATOMIC ABSORPTION SPECTROSCOPY: A STUDY  
OF THE MOLECULAR INTERFERENCES

BY

AHMED ELSAYED ABDELFATTAH

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in partial fulfillment of the requirements for the  
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1982

THE DETERMINATION OF LEAD BY ELECTROTHERMAL  
ATOMIC ABSORPTION SPECTROSCOPY: A STUDY  
OF THE MOLECULAR INTERFERENCES

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

David C. Hilderbrand      Date  
Thesis Advisor

David C. Hilderbrand      Date  
Head, Chemistry Dept.

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Abstract

The presence of interference effects in atomic absorption spectroscopy affects the degree of accuracy that can be obtained. A major source of interference in electrothermal atomization processes appears to involve the formation of molecular species. In the analysis of lead in the presence of chloride, three peaks are observed. The first of these peaks has an absorption spectrum characteristic of lead chloride. The second and third peaks cannot be identified on the basis of their respective spectra. In the presence of nitrate, the analysis of lead results in the presence of a broad band absorption profile that cannot be identified. The degree of molecular interference is dependent upon temperature, matrix concentration, graphite tube surface condition, the solution pH, and the wavelength used.

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## INTRODUCTION

Atomic absorption spectroscopy is a widely used method of analysis. Its rapid growth after the development of the first commercially available instrument was largely due to its reported relative freedom from interferences. In flame atomization systems, interferences for most elements are either small in magnitude or readily suppressed by the addition of appropriate matrix modifiers.

With the need for more sensitive methods of analysis, alternatives to flame atomization have evolved. The most successful of these atomizers have been the electrothermal graphite furnaces. Furnaces, however, are considerably more subject to interference, both chemical and physical. In the furnace, a sample is first dried to form a solid coating on the walls of the absorption cell. Further heating is used to selectively volatilize the organic constituents and the volatile inorganic matrix species. Finally, the temperature is rapidly raised to volatilize the species of interest and convert it to the atomic state.

The sensitivity observed for a given element is highly dependent upon the matrix used. A major contribution to the variation in intensity of the absorption signal observed for a given amount of analyte is the formation of molecular species involving the element of interest. This can lead to several potentially significant effects. The rate of volatility of the test metal varies with the anionic species. The test element may be volatilized in either the atomic or molecular state. When volatilized in the

molecular state, the molecule may fail to dissociate to yield the free atom required to absorb at the atomic line wavelength. Different matrix species may alter the tendency of the analyte element to form a carbide in the heated carbon furnace. Further, other metallic element species may compete with the analyte for molecular species formation. In addition to molecular formation interferences, the element of interest may be trapped in a low volatility matrix on the surface of the furnace. Several of these effects would occur under nonequilibrium conditions thereby increasing the difficulty in avoiding them.

An understanding of the factors which are actually causing the interferences to occur should lead to procedures for reducing or eliminating their effects. The most widely studied element in this respect is lead. However, the mechanisms involved in signal suppression or enhancement observed with varying matrices have not been elucidated. It is the purpose of this paper to further study interference effects on the analysis of various matrices for lead; in an attempt to gain a better understanding of the chemical and physical phenomena involved in atomization from the surface of a heated graphite furnace.



## DEFINITION AND HISTORICAL

### Definition

Atomic absorption and atomic absorption methods form a distinctive area of spectroanalysis. Samples are usually atomized by flame methods. There are other means of producing free atoms which may be used in a similar way for analysis, in the absence of flames. All of these areas of instrumental analysis are usually called atomic absorption spectroscopy. This term, which was introduced by Walsh, denotes any analytical method in which an element is atomized in order to permit the observation, selection and measurement of its absorption spectrum.(1,2)

The method could be defined in general terms as an instrumental spectro-analytical method which is based on the measurement of the absorption produced, in a beam of radiation of suitable wavelength proceeding from an emitting source of constant intensity, by a medium composed of atoms of the element to be determined. Under these conditions, the amount of absorption increases with the concentration of atoms in the absorbing medium, and thus with the concentration of the sample solution used in producing the absorbing medium. If the sample is used in solid form, the absorption measured will increase with the mass of the element in the solid sample, whether it be in its original condition or subjected to pretreatment.

The flame is the classical method of atomization from solutions. The most common flames are air/acetylene with a temperature of 2300°C and nitrous oxide/acetylene with a temperature of 2950°C. Absorption is generally measurable for concentrations greater than 0.01 µg/ml. The desired reaction is the dissociation of the salt into free atoms. This reaction is limited by numerous interactions. In addition, the products rapidly pass into the flame, so the lifetime of the atoms is very brief, a few thousandths of a second.

Other methods have been investigated for decomposing the analytical sample. Electrical heating in a furnace and an inert atmosphere, first studied by L'vov has been the most thoroughly studied. L'vov took a very small sample and converted it completely to an atomic vapor, integrating the absorbance pulse that was thereby generated. This technique has yielded some of the best detection limits in terms of absolute amounts with sensitivities in the picograms.

### Historical

The ultimate origins of the method are to be found in the observations of Fraunhofer on the solar spectrum and in the subsequent identification of the emission spectra of various elements discovered by Bunsen and Kirchhoff. Mention must also be made of the studies of the composition of the stellar atmospheres and the elucidation of atomic spectra.

However, as a definite point of departure, the independent publications of Walsh (3) and of Alkemade and Milatz (4,5) are of

the greatest importance. These publications demonstrated the effective potential of atomic absorption as a new and universal analytical tool in the instrumental field. After this start, some time passed before the appearance of the first applications and the descriptions of the first laboratories. The building of instruments for research was undertaken by various authors in Australia, New Zealand, Europe, South Africa and North America. It was these instruments and their analytical applications that first aroused widespread interest in the new method.

The history of atomic absorption spectroscopy has been discussed (1,2). The first furnace used to produce atomic vapors was that designed by King to vaporize carbon as well as other refractory compounds. In 1961, L'vov adapted this method for the production of atomic vapors for atomic absorption spectrometry.

Numerous types of furnaces for producing atoms by rapid volatilization of a small quantity of sample heated to high temperature quickly appeared. One of these is the Massmann carbon furnace used by Manning. The carbon filament is named as a function of its dimensions (carbon rod, graphite rod, mini-Massmann) and has been studied by West and Matousek. A tantalum strip placed into an inert atmosphere was studied by Takeuchi, Hwang and Riandey. More recently, Renshaw investigated a tantalum-clad carbon furnace. Other atomization methods are based on other forms of volatilization such as a hollow cathode and luminescent discharge, the laser (investigated by Mossoti, and electron bombardment (Rousselet). However,

the furnace has developed into the most widely used method of flameless atomization for atomic absorption analysis of samples of low concentrations of analyte.

## REVIEW OF INTERFERENCE STUDIES

As early as 1971, Boudin, G., et al., (6) examined the interferences in the use of the graphite furnace (King furnace) technique. Four types of interferences were considered: (i) physical effects (e.g., variation in distillation rate of elements), (ii) absorption by molecular species, (iii) formation of refractory compounds, and (iv) gas phase reactions of the elements. Most of the interferences were shown to be reduced or eliminated by the use of an optical system for background correction and a system for programming the temperature rise. The causes and mechanisms of chemical interferences in the condensed phase have been reviewed (7) and the effects of high salt content (8), various mineral acids (9), low concentrations of water, and miscible organic solvents (10) on the atomic absorption signal have also been considered. Atomization efficiencies for a number of elements in a graphite cuvette were measured by Nikolaev and Podgornaya (11). The extremely low atomization efficiencies found for chromium, vanadium, and titanium were explained on the basis of their formation of refractory carbide compounds. Siemer and Stone (12) found that the reduced sensitivity of nonresonance spectral lines is sometimes useful in the furnace atomic absorption determination of lead to prevent overload of read-out systems. Tantalum and molybdenum ribbon evaporators were compared by McIntyre, Cook and Boase (13). Although the molybdenum support could not be used at as high a temperature as tantalum, it did not become brittle and had an extended lifetime (1200 cycles).

In the determination of Co, Ni, and Cu, interelement effects were less for the molybdenum filament than for either tantalum or carbon. The authors also note that background radiation from any metal atomizer will be less than from carbon at the same temperature because of the lower emissivity of the metal.

The continuing problems of matrix interferences in electrothermal atomizers has led to several investigations of the rates and mechanisms of atom formation in carbon furnaces. Torsi and Tessari (14) found the release of Pb atoms in a  $H_2$  environment to follow a previously developed theory which assumes a monolayer or less coverage at the carbon surface and a first-order kinetic atom release process. Fuller (15, 16) has used a model which assumes a first-order reduction of the metal oxide at the carbon surface to examine the rate of atom formation and loss and atomization efficiency and discusses how atomization parameters might be adjusted to alleviate matrix problems. Atom loss from a constant temperature furnace (17) was found to occur via two different mechanisms: simple diffusion (Ag, Cd, Zn) or diffusion complicated by carbide formation at high temperatures (Mn, K, Cu). Frech and Cedergren (18, 19) have applied high temperature equilibrium calculations to explain the mechanism of a chloride interference on lead. For Pb analysis in steel samples (18, 19) addition of  $H_2$  to the sheath gas was found to aid in the removal of Cl (by forming HCl rather than  $PbCl$ ,  $PbCl_2$ , or  $FeCl_2$ ). For Pb analyses in NaCl matrices (20), both a high nonspecific absorption and a 20% loss in sensitivity over distilled water standards were observed.

Addition of  $\text{HNO}_3$  reduced the nonspecific absorption (evolution of  $\text{HCl}$  and  $\text{NaNO}_3$ ), but did not improve the sensitivity. Co volatilization of  $\text{Pb}$  was the postulated cause. Ottaway (21) maintains that although a reducing carbon surface can promote metal formation by reduction of the metal oxide, these reducing conditions do not exist at the atomizer surface. Therefore, salts which would volatilize before the reduction occurs are thermodynamically feasible and would be atomized only by a thermal decomposition process. Matrix salts such as chlorides which are volatile and do not decompose to an oxide would thus interfere more than oxyanions which can decompose to oxides. Yasuda and Kakiyama (22, 23) measured molecular spectra above a carbon tube atomizer at temperatures from 150 to 2600°C and found  $\text{SO}_2$  and  $\text{NO}_2$  from sulfate and nitrate solutions as well as undissociated metal halide spectra ( $\text{CrCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{MnF}_2$ ,  $\text{CuCl}$ ,  $\text{CoBr}_2$ , etc.) from halide matrices. Pritchard and Reeves (24), found alkali halide charge transfer spectra to comprise most non-atomic absorption with 3 different carbon atomizers (rod, cup, and tube). Only small (non-Rayleigh) scattering signals were observed.

It is evident that although a great deal of effort has been expended in elucidating the exact mechanism(s) of atom formation, universal agreement has not been reached. Results seem to show that the mechanism of atom formation differs according to several parameters. First, when different elements are compared, the differences in the mechanisms could be due to differing oxide stabilities, tendencies to volatilize or readiness to be reduced by carbon. Second,

the mechanism differs when different matrices are involved, for example, the chlorides and oxides or oxyanion species show marked differences. Third, the design of the atomizer differs according to the manufacturer and it controls the rates of heating, the containment volume, and atom loss mechanisms. The complexity of this problem is clearly manifested in the number of interferences observed for various matrices and in the number of procedures for minimizing or eliminating matrix effects. Czabic and Matousek (25) measured atomization temperatures in the presence of various anions. Only phosphate was found to change the appearance temperature and only for elements normally atomizing at temperatures lower than Sn. They conclude this observation supports two mechanisms of atom formation, reaction with carbon at low temperatures and thermal decomposition at higher temperatures. Numerous cations were found to interfere with determination of Fe, Co, and Ni (26). Although some degree of interference was noted for all cations, those having appearance temperatures near that of the analyte were most severe.

Ohta and Suzuki found that Pb signals are depressed in the presence of  $I^-$ ,  $NO_3^-$ , or carbamates (27). Ascorbic acid was found to yield both rhombic and tetragonal PbO when heated in a crucible with  $Pb(NO_3)_2$ . This was manifested in double peaks in the analysis of Pb in ascorbic acid solutions (28). Thompson, et al. (29) found that interferences for Pb and Cd could be minimized by coating the carbon tube with La.

Wegscheider, et al. utilized factorial experimental design



to determine interference effects on Pb, Cd, and Zn. They found that  $F^-$  and the cross term  $F^-/PO_4^{3-}$  interfered with Zn determinations and that these interferences were strongly dependent on ash time and temperature and that all mineral acids except HF interfered with Pb determinations (30). They also found that Co, Cr, Ni, Si, Hg, and Zn interfered with Pb and that an ash temperature of 900°C minimized the interferences. Anderson (31) found a severe interference of  $SO_4^{2-}$  on Pb could be eliminated by the addition of La to the analytical solution.

Czobic and Matousek (32) studied metal chloride interferences with a Varian CRA-63. Comparison of analyte atomization temperatures with time-resolved interferent population indicated that atomic population (i.e., of Pb) was depleted by chloride formation in the vapor phase. Manning and Slavin (33, 34) carried out a detailed study of the determination of Pb in a chloride matrix with a graphite furnace. Pb is the most frequently determined element by electrothermal atomization and chloride is perhaps the main problem interferant. They obtained best results when a short atomization ramp was used, peak areas were determined, Mo coated pyroelectric tubes were used and  $NH_4NO_3$  was added as a matrix modifier.

Hageman, et al., (35, 36) carried out two studies in which pulse-type electrothermal atomizers (i.e., most commercial systems) were compared to constant temperature furnaces (i.e., "Woodriff"-type furnace). The most common matrix effects (i.e., high  $Cl^-$ ) were minimal with the constant temperature furnace compared to the pulse-

type atomizers. Krasowski and Copeland (37) also compared Varian type electrothermal atomizers to the Woodriff furnace for the determination of Cd, Cr, Cu, and Pb with NaCl, NaClO<sub>4</sub>, and NH<sub>4</sub>Cl interferences. Interferences of 5% suppression with the Woodriff furnace were often as serious as 80% with the more conventional atomizers.

Regan and Warren (38, 39) noted the effect of ascorbic acid and graphite tube condition on the determination of Pb. Nakamura and Kawase (40) discussed errors of background correction by a deuterium lamp in atomic absorption spectrometry. Relative lamp alignment problems, differences in spatial and time behavior of the background, and analyte signals were discussed.

Maney and Luciano (41) studied the effects of K, B, Ca, Mg, and Cl on the time evolution of the Pb absorption signal. Salmon, et al., (42) felt that chemisorbed O<sub>2</sub> caused time shifts and double peaks for Pb. Two active sites on the carbon surface were suggested which could be altered by O<sub>2</sub>.

Lawson and Woodriff (43) indicated that in addition to chemical modifications, selective volatilization, and standard addition methods, atomizer design was important for the reduction of matrix interferences. Matousek (44) discussed the elimination and control of interferences in electrothermal atomization atomic absorption spectrometry.

Another means of reducing matrix interferences is by physically altering the graphite tube atomizer to achieve more isothermal

conditions during analyte atomization. Two approaches most often used are introduction of the sample into a specially constructed constant temperature furnace and atomization of the sample from a platform placed within the graphite tube of a commercially available atomizer.

Recently, the combination of chemical modifiers and the platform has largely eliminated interferences on the Pb signal in various matrices. Kaiser, et al., (45) used  $\text{NH}_4\text{H}_2\text{PO}_4$  and a modified L'vov platform to greatly reduce Pb signal suppression during analysis of natural water. May and Brumbaugh (46) extended the use of  $\text{NH}_4\text{H}_2\text{PO}_4$  and a modified L'vov platform to eliminate interferences in the analysis of fish tissues for Pb.

Erspamer, J.P., and Niemczyk, T.M. (47) studied the volatilization of  $\text{PbCl}_2$ ,  $\text{MgCl}_2$  and  $\text{NH}_4\text{Cl}$  matrices as a function of graphite surface type in graphite furnace atomic absorption spectrometry. The authors used pyrolytic and nonpyrolytic graphite tubes with each matrix and suggested that the type of the surface controls the ashing efficiency which could be responsible for the difference in spectra obtained, notably with  $\text{MgCl}_2$ .

Virtually all manufacturers of atomic absorption instrumentation offer simultaneous background correction systems based on the continuum lamp described by Koirtiyohann and Pickett (48). However, background correction using continuum sources has limitations. The combined effect of the limitations results in possible errors due to under or over compensation for the background signal. The need for

improved background correction capability generated interest in applying the Zeeman effect to atomic absorption spectrometry. In 1971, Hadeishi and McLaughlin (49) first reported the application of the Zeeman effect to the determination of mercury. Most of the work that followed concentrated on the theoretical aspects until Fernandez, Myers and Slavin (50) investigated the instrumental application of the Zeeman effect. They employed a versatile Zeeman test instrument, capable of both flame and furnace operation and compared its performance to the conventional atomic absorption with respect to sensitivity, analytical range, and background correction. Out of forty-four elements, only four elements showed a loss of sensitivity exceeding a factor of two for the Zeeman-effect instrument.

## EXPERIMENTAL

### Apparatus

Atomic and molecular absorptions were measured with a Perkin-Elmer 2380 atomic absorption spectrometer combined with HGA-400 graphite furnace. A deuterium lamp was used for background correction with the atomic absorption measurements and as a continuum light source for the molecular absorption measurements. Eppendorf micropipettes were used to place test solutions in the atomizer. Both pyrolytic and non-pyrolytic graphite tubes were used. All glassware was cleaned by washing with 3 N nitric acid and then rinsing with deionized water until neutral.

### General Procedure

The recommended optimal instrumental conditions for electrothermal determination of lead were followed. The test solution (20  $\mu$ l) was placed in the atomizer, dried for 5 S. at 110°C, ashed for 5 S. at 500°C, and atomized for 5 S. at 2100°C. The ramp time of the drying, ashing and atomization was 5, 5 and 1 second respectively. Other temperatures, hold and ramp time settings used for atomic and molecular absorption measurements are described in the appropriate sections. Argon gas was used as the inert purge gas at a flow rate of 90 ml min<sup>-1</sup>. The stop flow mode was used in the molecular absorption measurements which permits the internal purge gas stream to be interrupted and enhances the absorption signal. The read out was in absorbance for the atomic and molecular measurements. Each single reported reading is the mathematical mean of at least three

readings of three sample injections into the instrument. The percent enhancement or suppression was calculated by the following formula:

$$\% \text{ S.E. or S.S.} = \frac{\bar{A}_a - \bar{A}_b}{\bar{A}_b} \times 100\%$$

where  $A_a$  is the absorbance in the presence of interferent and  $A_b$  is the absorbance in the absence of interferent. All solutions were prepared from reagent-grade chemicals. Deionized water and 0.2% nitric acid were used as diluents. The water was used in preparing the solutions of the interferents and lead nitrate stock solution of 1000 ppm lead. The 0.2% nitric acid was used in preparing the lead reference standards when needed. The 0.2% nitric acid was prepared from reagent-grade concentrated nitric acid diluted with deionized water.

### Operations

1. The extent of alkali and alkaline earth halide matrix interference on lead absorbance was observed. A solution of 0.25 ppm lead, calculated as lead, was prepared from the lead stock solution with 0.2% nitric acid as the diluent. This solution was used as a reference standard relative to the interferents. The salts used as interferents were LiCl, NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>. The concentration of the interferents were 50, 100, 200, 300 and 500 ppm each. Solutions of NaCl and NaBr of 50 ppm each were prepared. Calculation was based on sodium. Their absorbances were

measured and compared with the absorbance of a lead reference standard sample of 0.25 ppm.

2. The role of the metal cation in the interference process was studied. Sodium and potassium nitrate and sodium carbonate were selected. The oxide is the anticipated decomposition product of each salt. The sodium and potassium nitrate solutions were prepared in different concentrations to provide two sets of experiments. The first was a solution of 50 ppm, calculated as the cation in sodium or potassium nitrate. Each solution contained 0.5 ppm lead. Two types of solutions were prepared, one by dissolving the salt in deionized water, and the other by dissolving the salt in 0.2% nitric acid. The absorbance of each solution was measured and compared to the absorbance of a reference solution of 0.5 ppm lead only. The second set of solutions contained 50 or 500 ppm sodium from sodium nitrate. Each solution contained 0.5 ppm lead. Its absorbance was compared to that of 0.5 ppm lead only. Two types of tubes were used, the pyrolytic and the non-pyrolytic. Solutions containing 0.5 ppm lead, 500 ppm sodium and 0.2% nitric acid were also studied in both types of tubes. A similar set of experiments was repeated using solutions of sodium carbonate in concentrations of 50 and 500 ppm, calculated as sodium.

3. Two parameters were investigated to observe the influence of the chloride ion on the lead absorption signal. These parameters were the atomization temperature and the tube surface type. Solutions of 0.5 ppm lead and hydrochloric acid in concentrations of 50, 250,

300 and 10,000 ppm were prepared. The calculation was based on the chloride ion. Reagent-grade concentrated acid was used in preparing the lower concentrations.

4. The role of the test solution pH was investigated by observing the extent of sodium chloride interference on lead in both acidic and alkaline media relative to a neutral medium. The lead and sodium chloride concentrations were 0.5 and 50 ppm respectively. The alkaline solution was prepared using sodium hydroxide in 50 ppm concentration. The acidic solution was prepared using hydrochloric acid at 50 ppm.

5. The extent of interference on lead by sodium chloride and sodium hydroxide was observed at two different lead absorption lines 283.3 and 217.0 nm. Solutions of 0.5 ppm lead, 50 ppm sodium chloride and 50 ppm sodium hydroxide were prepared. The calculations used for preparing the sodium chloride and hydroxide were based on sodium.

6. The molecular absorption spectra of lead chloride and lead nitrate were measured at selected wavelengths; 190, 200, 225, 250, 275, 283.3, 300, 325, 350, 275, and 390 nm. The spectra were monitored at selected wavelengths due to the transient nature of the absorption peak. The deuterium lamp was used as the continuum light source. The instrument was set to the background only mode which automatically shuts down the single element lamp if it were on. The spectra were obtained by monitoring the absorbance read out at each wavelength. The slit width for all the measurements was still 0.7 nm.



Sample volumes were 50  $\mu\text{L}$  for all the measurements. The atomization temperature was 2100°C.

A solution containing 1000 ppm lead as lead chloride, and another solution containing 1000 ppm lead as lead nitrate were prepared using deionized water. The absorption spectrum for each solution was measured using both the pyrolytic and the non-pyrolytic tubes. Another set of solutions was prepared. Measurements of the absorption spectra of solutions containing 500, 1000, and 2000 ppm lead as lead chloride, were taken. The pyrolytic tube only was used. All the solutions were prepared by dissolving the lead salt in deionized water.

The solution containing 1000 ppm lead as lead chloride was selected to measure the molecular absorption spectra at different atomization temperatures, 2100, 2500, and 2700°C. The wavelength selected was 275 nm which previously showed strong absorbance. The drying and ashing set up remained the same as in the previous measurements; 110°C, 15 S., 5 S., for the drying temperature, ramp, and hold respectively. Then 500°C, 5 S., 5 S., for the ashing temperature, ramp, and hold respectively. Only the pyrolytic tube was used. The sample volume 20  $\mu\text{L}$  was used for all measurements. The slit width remained 0.7 nm.

The terminology of lead chloride refers to a species composed of lead and chlorine with an undefined stoichiometric ratio.

## RESULTS AND DISCUSSION

### Extent of Interference

The extent of interference on lead in alkali and alkaline earth halide matrices was observed. The interferent concentration varied while that of the lead was constant. The results are summarized in Table 1. The alkali metal chlorides resulted in a relatively constant percent signal suppression with increasing interferent concentration. The alkaline earth metal chlorides increase the percent signal suppression with increasing interferent concentration.

Sodium chloride was chosen as an interferent with a constant concentration while the lead concentration was increased. The same work was performed using some bromide as an interferent. The results are summarized in Table 2. The percent signal suppression for each salt was relatively constant as the lead concentration increased.

### The Role of the Metal Cation

The effects of the presence of selected sodium and potassium salts were studied. The percent signal suppression using deionized water as a diluent and sodium nitrate as an interferent was 58.5. Using nitric acid as a diluent, a signal enhancement of 22.1% was observed. This illustrates the importance of the presence of the metal cation relative to the anion in causing a serious suppression of the signal. However, when the nitric acid was used as a diluent and the sodium nitrate was added as an interferent, the percent signal suppression was 65.6, that is more than with the salt only. The

Table 1. Lead<sup>\*</sup> Signal Suppression with Metal Chlorides

	Matrix Salt				
	LiCl	NaCl	KCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>
ppm <sup>***</sup> salt	%S.S. <sup>**</sup>	%S.S.	%S.S.	%S.S.	%S.S.
50	77.6	55.8	25.1	10.5	14.3
100	78.9	60.1	40.3	24.8	31.4
200	79.6	57.1	40.3	57.1	62.9
300	69.1	55.8	41.5	67.6	85.7
500	77.6	57.1	39.8	61.0	100.0

\* All the solutions contained 0.25 ppm lead.

\*\* %S.S. means percent signal suppression.

\*\*\* Calculated as the metal.

Table 2. Lead Signal Suppression with Sodium Chloride and Bromide.\*

Pb, ppm	Matrix Salt	
	NaCl	NaBr
	%S.S.	%S.S.
0.1	55.2	64.0
0.2	57.5	49.4
0.3	57.9	47.8
0.5	55.8	49.4

\* All the solutions of sodium chloride and bromide contained 50 ppm of the salt, calculated as sodium.

role of the acid in the increased signal suppression in the latter case is unclear. The same pattern was observed on using potassium nitrate as an interferent.

The role of the sodium metal cation was further investigated by using sodium nitrate as an interferent in two concentrations, 50 and 500 ppm. The effect of the two types of the graphite tubes, the pyrolytic and non-pyrolytic was observed. The results are shown in Table 3. The use of the pyrolytic tube confirmed the signal suppression. However, the use of the non-pyrolytic tube resulted in a signal enhancement.

The influence of the nitric acid on the signal suppression caused by sodium nitrate and the signal enhancement obtained on using a non-pyrolytic tube demonstrate a possibility for a numerous-interference mechanism. The extent and direction of interference caused by sodium nitrate appears to be governed by the solution pH and surface condition of the graphite tube.

The data in Table 4 indicates a smaller enhancement of the lead signal by sodium nitrate in the presence of the nitric acid when the non-pyrolytic graphite tube was used. This demonstrates the importance of the surface type compared to the solution's pH. More research is needed to explain the cause(s) of the signal enhancement.

A similar approach was used with sodium carbonate as an interferent. The results are shown in Table 5. A consistent

Table 3. Pb Absorbance in the Presence of  $\text{NaNO}_3$ .

Tube		Blank	Pb Only*		50 ppm $\text{NaNO}_3$	500 ppm $\text{NaNO}_3$
			Before	After		
Pyrolytic	Abs.	.016	.144	.152	.091	.072
	%S.S.	----	----	----	38.5	51.4
Non-Pyrolytic	Abs.	.008	.176	.175	.205	.202
	%S.E. **	----	----	----	16.5	14.8

\* The lead reference standard solutions contained 0.5 ppm Pb.

\*\* %S.E. means percent signal enhancement.

Table 4. Pb Absorbance in the Presence of  $\text{NaNO}_3$  and  $\text{HNO}_3$ .

Tube		Blank	Pb Only		500 ppm $\text{NaNO}_3$ without $\text{HNO}_3$	500 ppm $\text{NaNO}_3$ with $\text{HNO}_3$
			Before	After		
Pyrolytic	Abs.	.005	.165	.160	.092	.081
	%S.S.	----	----	----	43.6	50.3
Non-Pyrolytic	Abs.	.008	.141	.152	.201	.182
	%S.E.	----	----	----	36.7	23.8

Table 5. Pb Absorbance in the Presence of  $\text{Na}_2\text{CO}_3$ .

Tube		Blank	Pb Only*		50 ppm $\text{Na}_2\text{CO}_3$	500 ppm $\text{Na}_2\text{CO}_3$
			Before	After		
Pyrolytic	Abs.	.008	.143	.146	.156	.166
	%S.E.	----	----	----	7.3	14.5
Non-Pyrolytic	Abs.	.002	.164	.183	.170	.205
	%S.E.	----	----	----	----	17.8



signal enhancement was observed with both the pyrolytic and the non-pyrolytic tubes, and with increasing the salt concentration. The percent signal suppression or enhancement was calculated relative to the mathematical mean of the lead signals before and after running the samples containing the interferent.

#### The Role of the Chloride Anion

The effects of the presence of the chloride anion were investigated in the absence of the alkali or the alkaline earth metal cation. Hydrochloric acid (HCl) was used in concentrations of 50, 250, 300 and 10,000 ppm chloride. The lead concentration was 0.5 ppm. The atomization temperature was varied to observe its influence on the lead signal in the presence of the chloride anion. Results are summarized in Table 6. Experimentally, the 1900°C atomization temperature resulted in the largest absorption signal in the absence of the interferent, while the 2100°C was the only atomization temperature to result in a signal enhancement in the presence of the interferent.

This study was extended to compare the effect in the two types of graphite tubes. Both low and high concentrations of chloride were used. Results are summarized in Tables 7 and 8. The performance of the pyrolytic tubes varied widely under similar experimental conditions, while the non-pyrolytic tubes gave more consistent results. The use of the pyrolytic tubes gave large signal suppression with 10,000 ppm chloride while the non-pyrolytic tubes did not. The lead signal decreased after running the samples with the

Table 6. Pb Absorbance at Different Atomization Temperatures.

Solution	Atomization Temperatures			
	1900	2100	2300	2700
Pb, 0.5 ppm	.204	.160	.183	.188
+50 ppm Cl <sup>-</sup>	.109	.187	.163	.121
+300 ppm Cl <sup>-</sup>	.123	.167	.170	.091

Table 8. The Function of the Non-Pyrolytic Tubes in the Presence of HCl.

Tubes	Sample	Blank	0 Interferent <sup>*</sup>		+50 ppm Chloride <sup>**</sup>	+250 ppm Chloride	+1000 ppm Chloride	+10,000 ppm Chloride
			Before	After				
Tube #1	Abs.	.015	.220	.244	.218	.217	.224	.215
	%S.S.	----	----	----	5.6	6.1	3.0	6.9
Tube #2	Abs.	.009	.179	.188	.182	.175	.177	.172
	%S.S.	----	----	----	1.1	4.9	3.8	6.5

\* All samples except blank contain 0.5 ppm lead.

\*\* Chloride was presented as HCl.

interferent on using the pyrolytic tubes while the reverse was observed with the non-pyrolytic tubes. From these observations, it appears that a change in the surface conditions of the pyrolytic tubes on using the acid in high concentrations is occurring.

#### The Role of the pH

The interference in the presence of the hydrochloride acid is less than in the presence of sodium chloride using non-pyrolytic tubes. The effect of the solution's pH was tested on salt interference. The selected concentration of sodium chloride was 50 ppm and the solution pH was 5.7. A lead solution containing sodium chloride and sodium hydroxide at a concentration of 50 ppm each and with a pH of 11.0 was used. The lead concentration in the two solutions was 0.5 ppm. Since the percent signal suppression was similar for the two solutions, the large difference in the solution's pH was not significant.

The sodium chloride interference was observed in the presence and absence of the hydrochloric acid. The concentration of each was of 50 ppm, the solution's pHs were 2.9 and 5.7 respectively. The percent signal suppression in the presence of the acid was 53.0% compared to sodium chloride alone which was 40.7%. This suggests an influence of the solution's pH on the extent of the interference mechanism with solutions of highly acidic pHs.

#### Selection of the Wavelength

The lead absorption line at 283.3 nm is recommended by the instrument's manufacturers as the most sensitive for atomic absorption

analysis. However, a check of the absorption line at 217 nm was considered. Samples of lead solutions with conc. 0.5 ppm lead and having sodium chloride and sodium hydroxide as interferants with a concentration of 50 ppm each, were analyzed using the two lines. As shown in Table 9, under the given conditions, the wavelength at 217 nm evidently resulted in more lead sensitivity relative to the wavelength at 283.3 nm in the presence and absence of the sodium chloride as an interferant but resulted in almost the same sensitivity with sodium hydroxide as an interferant.

#### Molecular Absorption Spectra

Since the background absorption is one of the primary interferences encountered in analyses for trace elements in heavy matrices, the absorption spectra that covered a wavelength range between 190 and 390 nm were measured for lead chloride and lead nitrate. The absorption spectra for lead chloride when vaporized from pyrolytic and non-pyrolytic surfaces are shown in Figures 1 and 2. The results in Figures 1 and 2 are in good agreement with the vapor phase spectra of lead chloride measured by Yasuda and Kakiyama (51) and Erspamer and Niemczyk (47). Evidently the change of surface conditions had little effect on the observed spectra. Each curve represents the mathematical mean of the results obtained with three tubes. The dashed plots in Figures 1 and 2 were observed in the first set of tubes. The others gave similar results and for the sake of clarity of the plot are omitted. The absorption spectra of lead nitrate were measured using the pyrolytic and

Table 9. Lead Absorbance at 283.3 and 217 nm.

$\lambda$ , nm	Blank	Pb Only <sup>*</sup>	+NaCl <sup>**</sup>	+NaOH <sup>**</sup>
283.3 nm	---	.236	.140	0.078
217.0 nm	---	.249	.194	0.077

\* All samples except blank contain 0.5 ppm lead.

\*\* 50 ppm of the salt, calculated as sodium.



Faint caption text at the bottom of the page, likely describing the graph above. It appears to mention 'Lead absorbance spectrum, resulting from lead chlor...'.

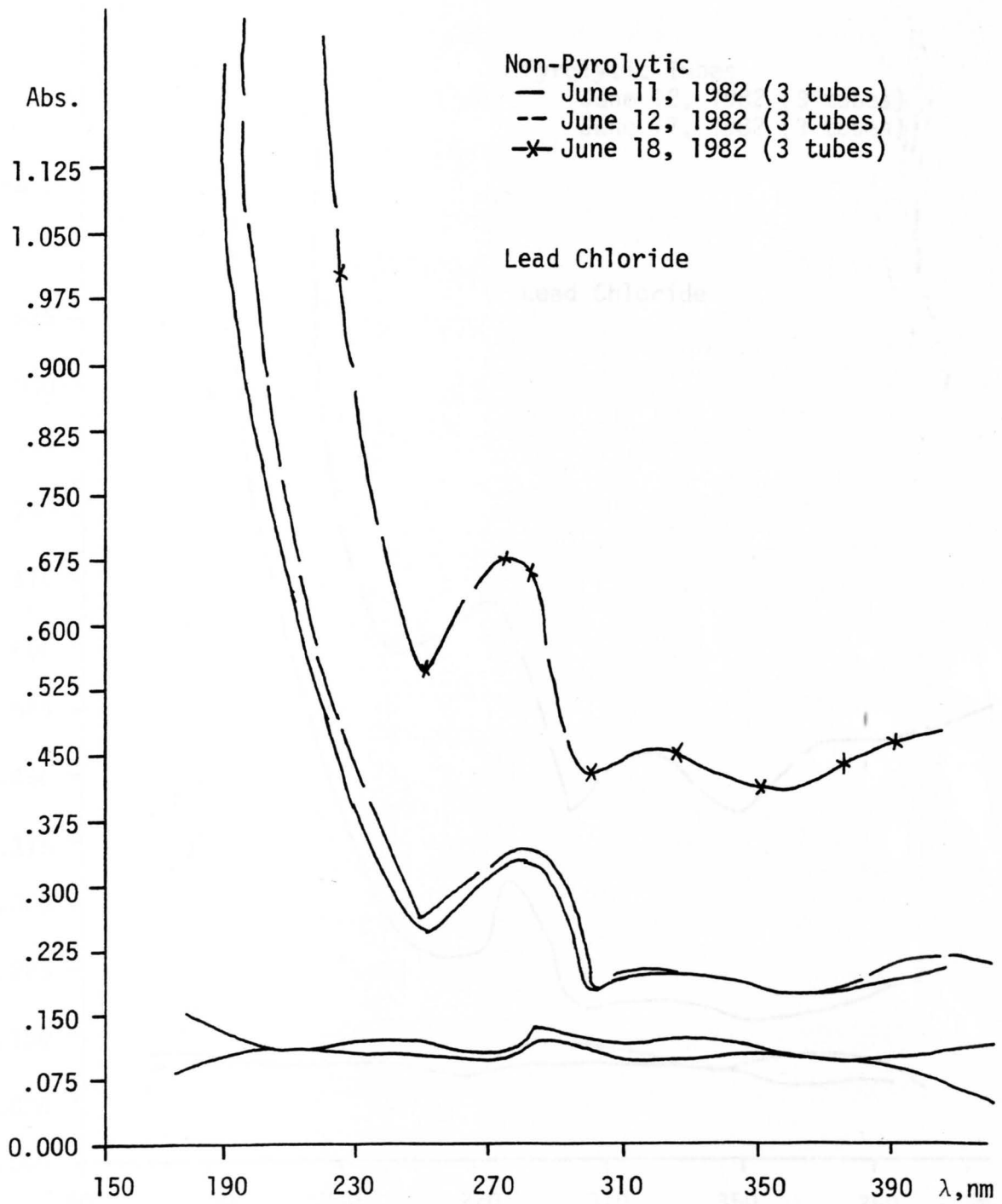


Figure 1. Broad band absorption spectrum resulting from lead chloride samples, non-pyrolytic tubes.

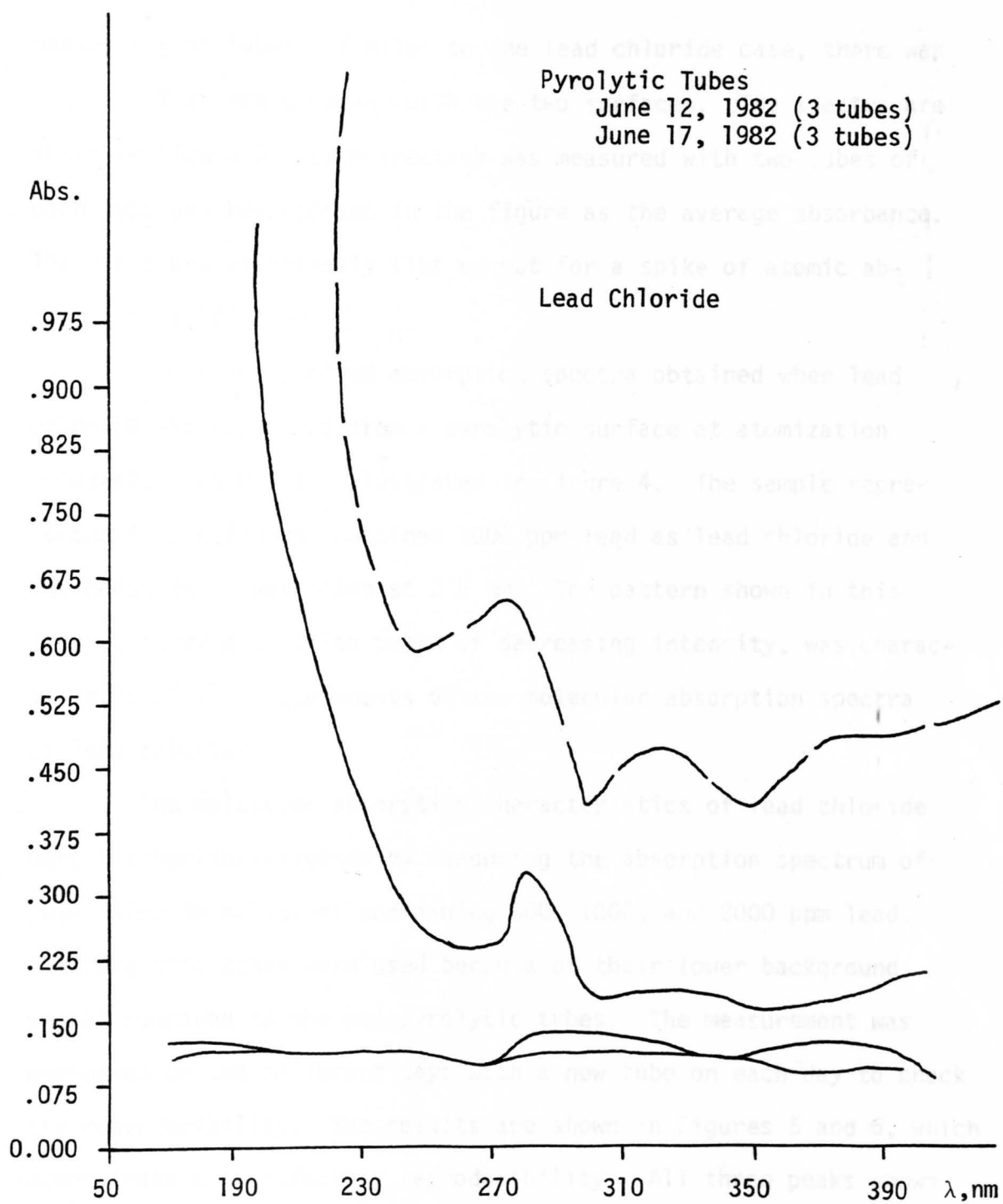


Figure 2. Broad band absorption spectrum resulting from lead chloride samples, pyrolytic tubes.



non-pyrolytic tubes. Similar to the lead chloride case, there was little difference observed with the two surfaces. The spectra are shown in Figure 3. Each spectrum was measured with two tubes of each type and represented in the figure as the average absorbance. The plots are essentially flat except for a spike of atomic absorption at 283.3 nm.

The time resolved absorption spectra obtained when lead chloride was vaporized from a pyrolytic surface at atomization temperature 2500°C is illustrated in Figure 4. The sample represented in the figure contained 1000 ppm lead as lead chloride and the measurement was taken at 275 nm. The pattern shown in this figure, three absorption peaks of decreasing intensity, was characteristic of all measurements of the molecular absorption spectra of lead chloride.

The molecular absorption characteristics of lead chloride were further investigated by measuring the absorption spectrum of lead chloride solutions containing 500, 1000, and 2000 ppm lead. The pyrolytic tubes were used because of their lower background signal compared to the non-pyrolytic tubes. The measurement was performed on two different days with a new tube on each day to check the reproducibility. The results are shown in Figures 5 and 6, which demonstrate a satisfactory reproducibility. All three peaks shown in the time-resolved curve of Figure 4 are lead related. A characteristic calibration curve can be obtained for each of the three peaks indicating that the intensity is related to the concentration

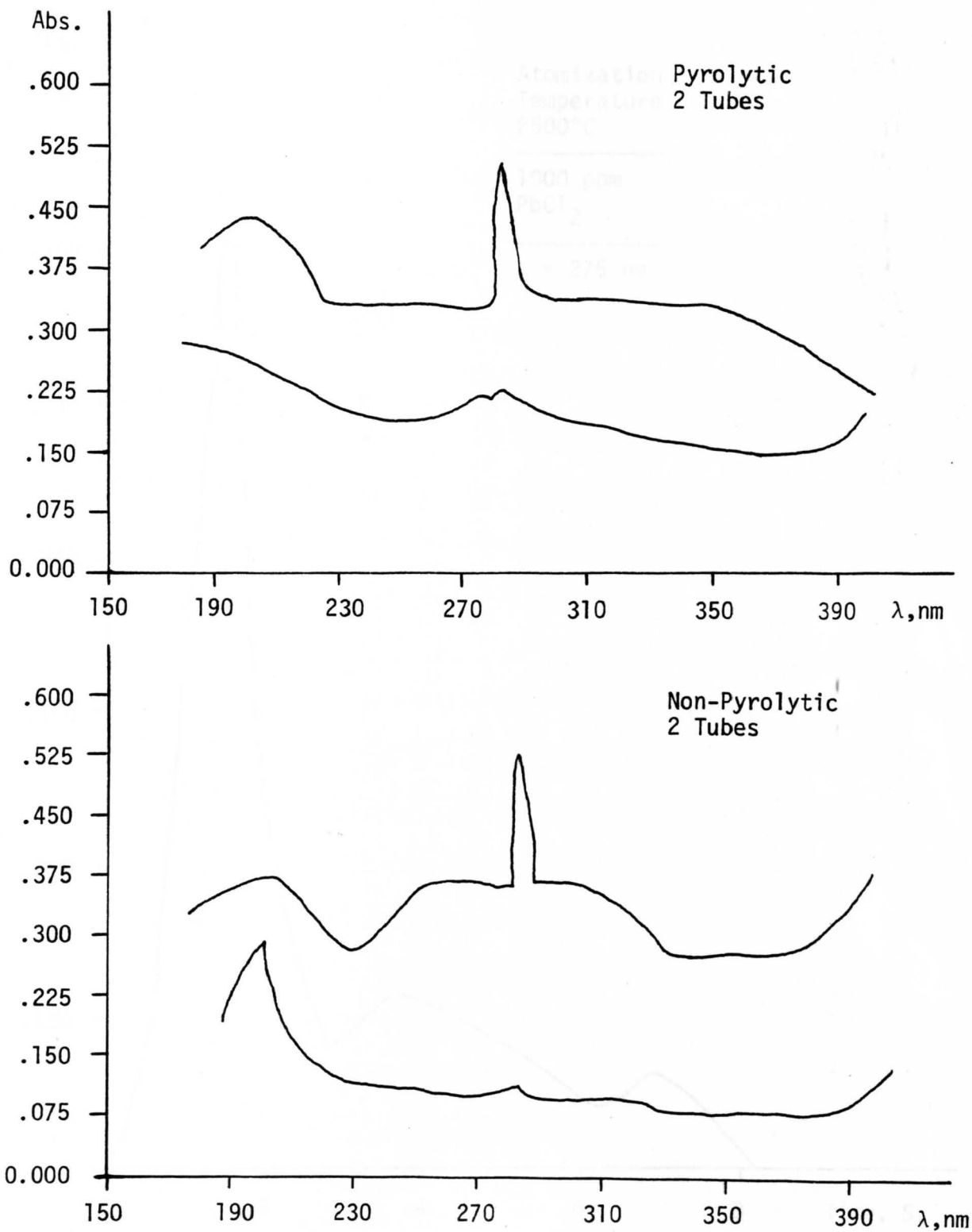


Figure 3. Broad band absorption spectrum resulting from lead nitrate samples.

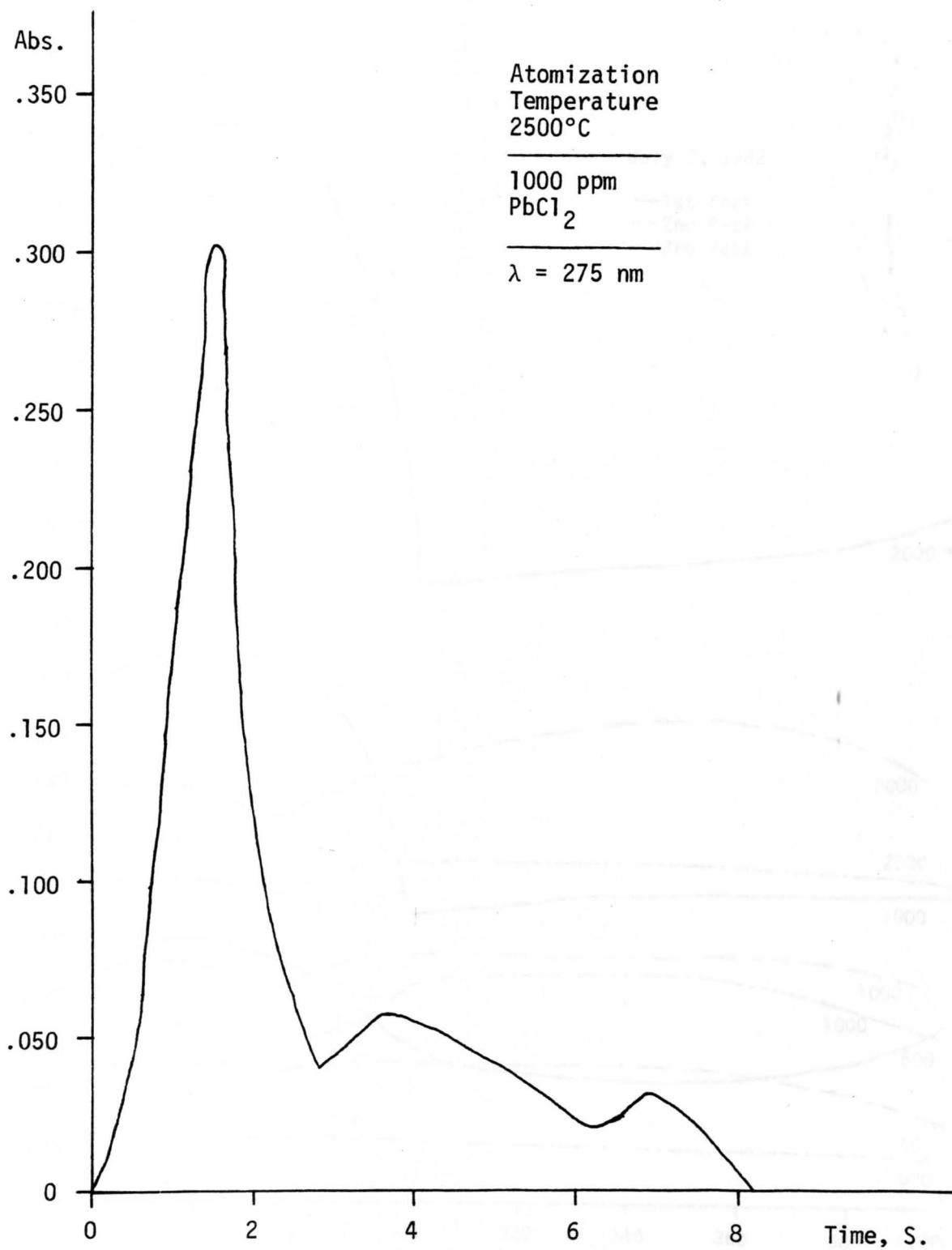


Figure 4. Variation in lead chloride sample absorption with time.

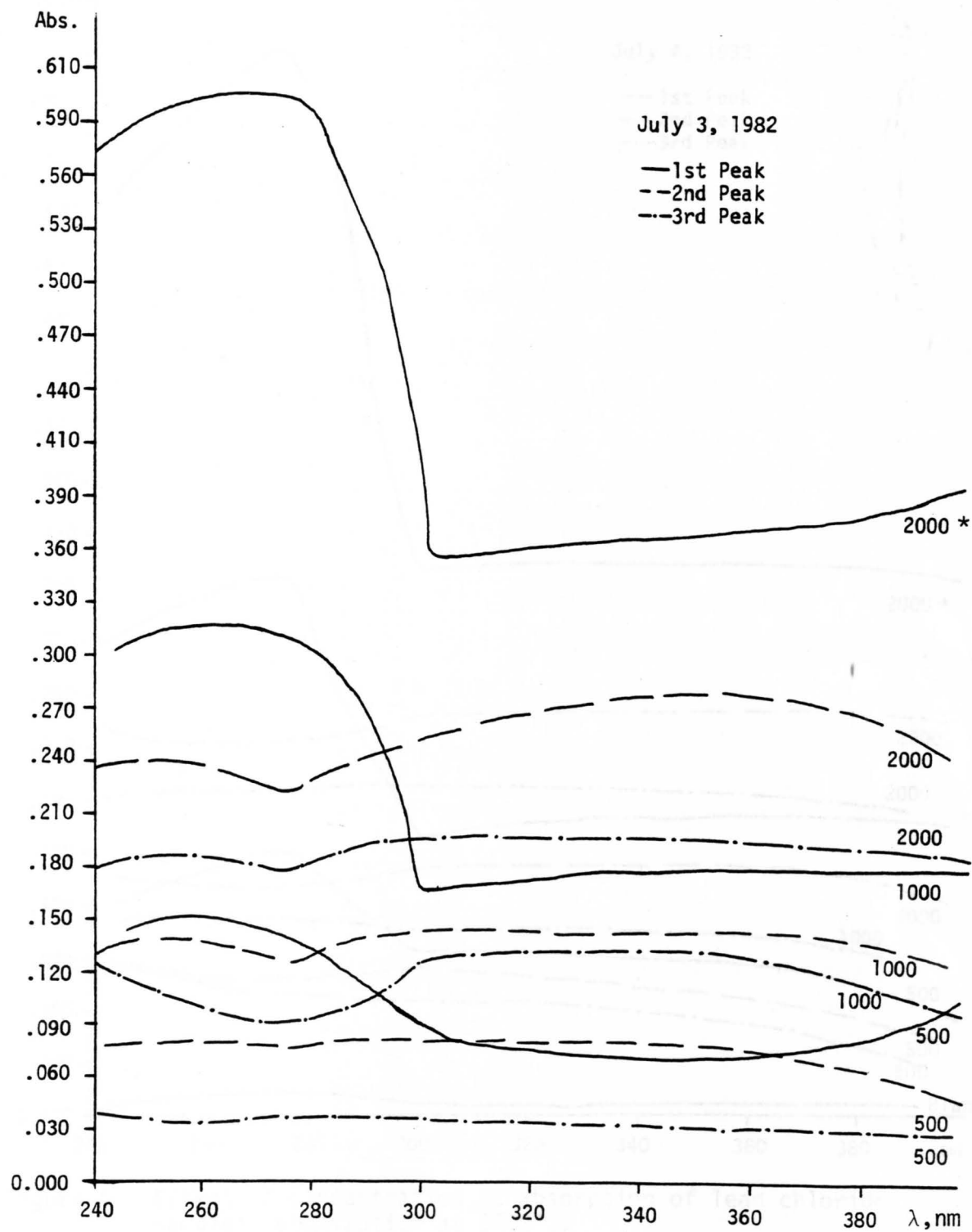


Figure 5. Effect of concentration on absorption of lead chloride samples.  
 \*Concentrations shown in ppm.

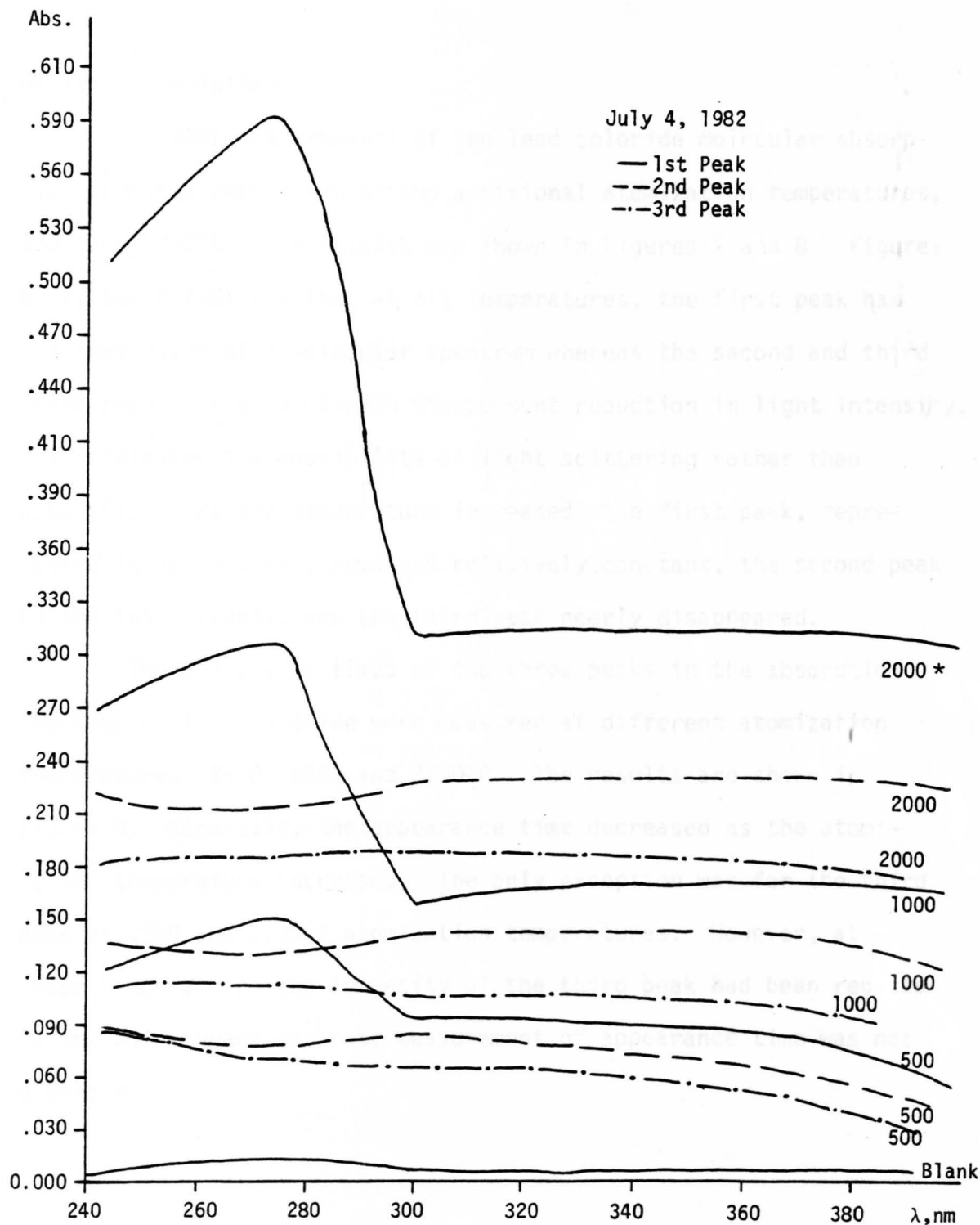


Figure 6. Effect of concentration on absorption of lead chloride samples, atomization at 2100°C.  
 \*Concentrations shown in ppm.

of lead in solution.

Further measurements of the lead chloride molecular absorption spectrum were taken at two additional atomization temperatures, 2500 and 2700°C. The results are shown in Figures 7 and 8. Figures 6, 7, and 8 indicate that at all temperatures, the first peak has the appearance of a molecular spectrum whereas the second and third peaks result in a wavelength independent reduction in light intensity. This indicates the possibility of light scattering rather than absorption. As the temperature increased, the first peak, represented in solid lines, remained relatively constant, the second peak became less intense, and the third peak nearly disappeared.

The appearance times of the three peaks in the absorption spectrum of lead chloride were measured at different atomization temperatures, 2100, 2500 and 2700°C. The results are shown in Figure 9. Generally, the appearance time decreased as the atomization temperature increased. The only exception was for the third peak at 2500 and 2700°C atomization temperatures. However, at these temperatures the intensity of the third peak had been reduced to the point where accurate measurement of appearance time was not possible.

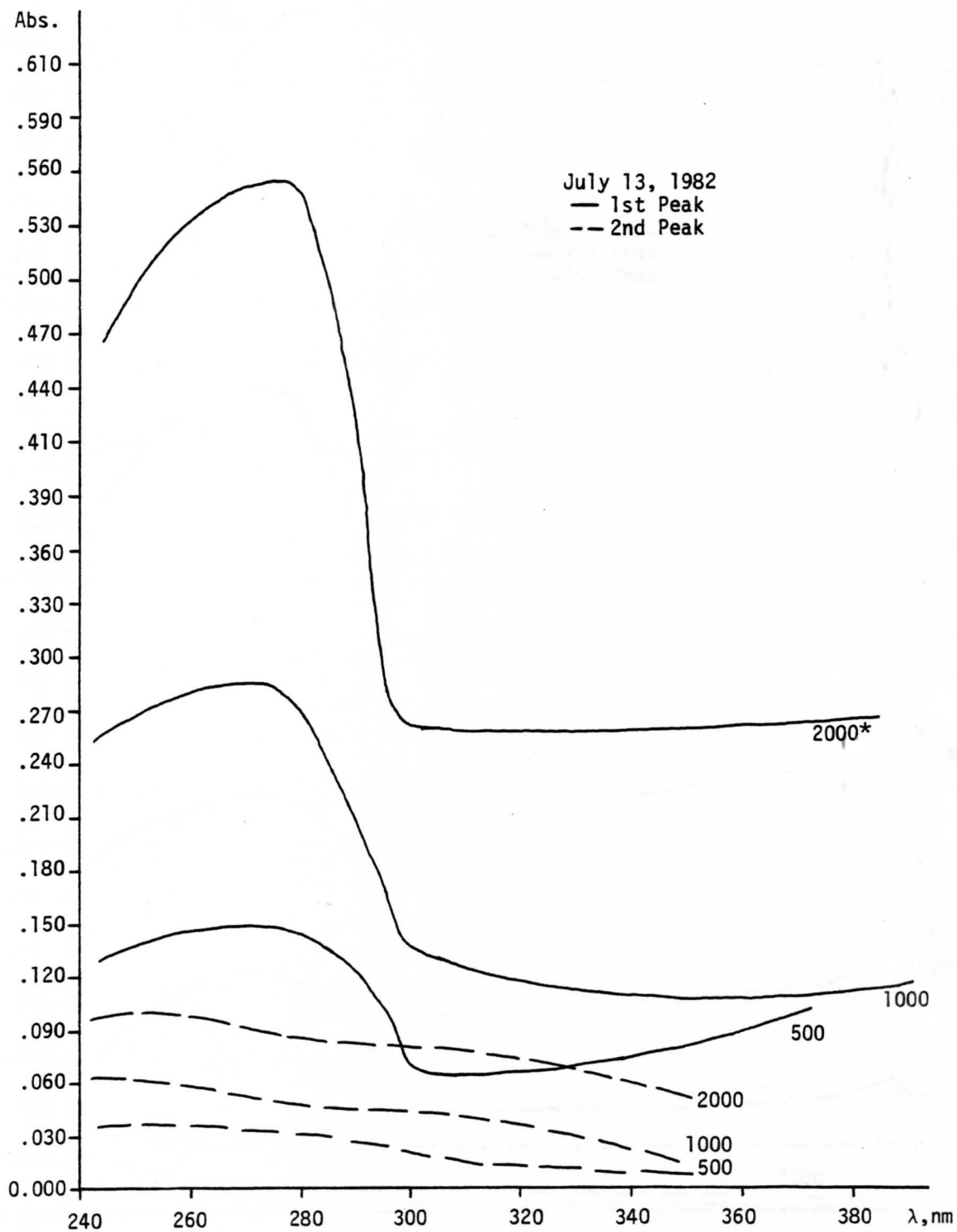


Figure 7. Effect of variation of temperature on the lead chloride absorption spectrum, atomization at 2500°C.  
\*Concentrations shown in ppm.

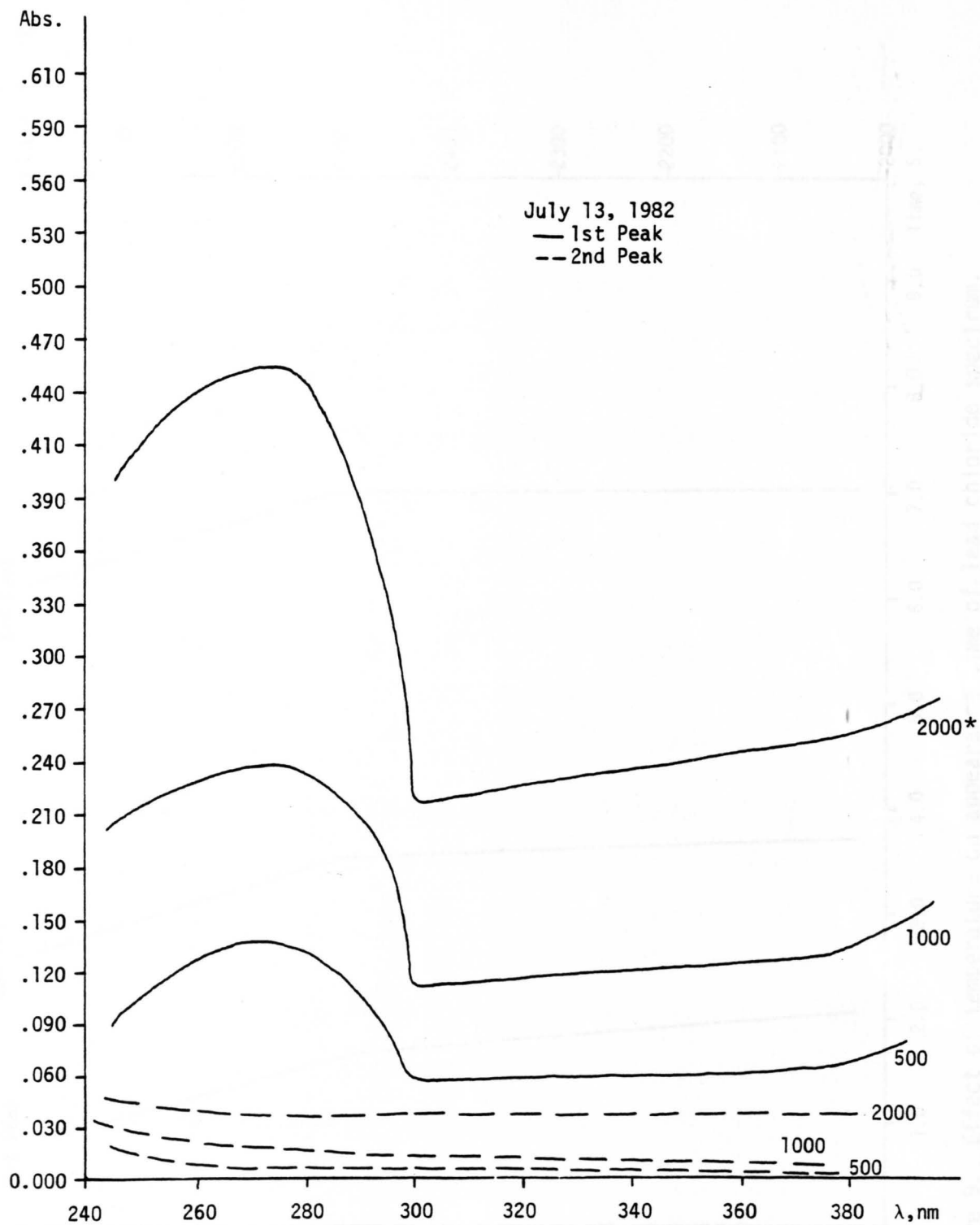


Figure 8. Effect of variation of temperature on the lead chloride absorption spectrum, atomization at 2700°C.  
\*Concentrations shown in ppm.



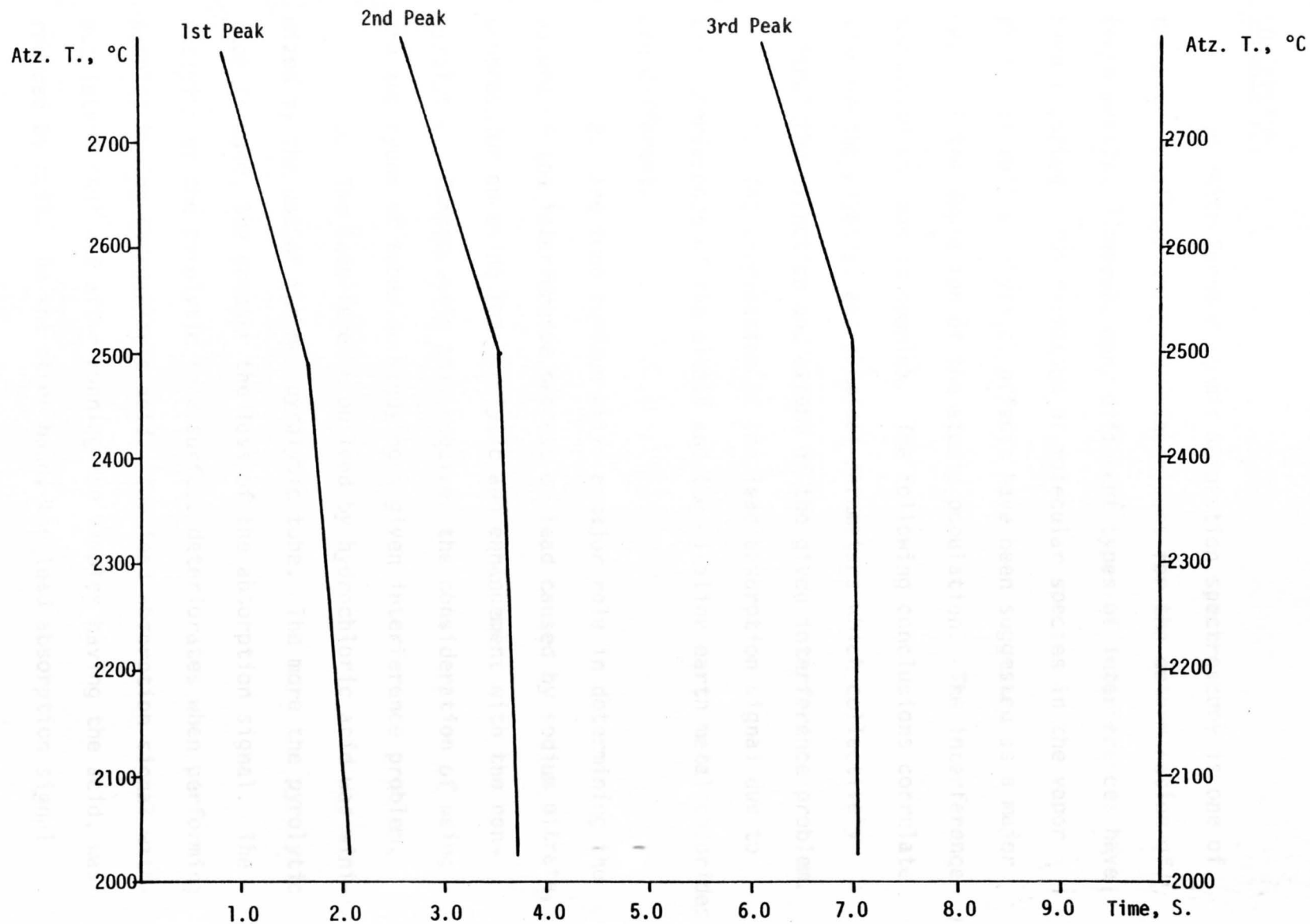


Figure 9. Effect of temperature on appearance time of lead chloride spectrum.

## CONCLUSIONS

Graphite furnace atomic absorption spectroscopy is one of the most sensitive analytical techniques for the determination of trace metals. However, many different types of interferences have been reported. The formation of molecular species in the vapor phase, as well as physical effects have been suggested as a major cause of the depletion of the atomic population. The interference mechanism on lead is complex. The following conclusions correlate some of the physical and chemical parameters which collectively control the direction and extent of the given interference problem.

1. The suppression of the lead absorption signal due to the interference of the alkali and the alkaline earth metal chlorides are different.

2. The tube surface plays a major role in determining the nature of the interference process on lead caused by sodium nitrate, suppression on using the pyrolytic and enhancement with the non-pyrolytic. Consequently this requires the consideration of using the two types of tubes on studying a given interference problem.

3. The interference on lead by hydrochloric acid was minimized by the use of the non-pyrolytic tube. The more the pyrolytic tube is used, the greater the loss of the absorption signal. The activity of the pyrolytic tube surface deteriorates when performing samples having hydrochloric acid. The lead absorption signal without interferent and after running the samples having the acid, was reduced by 8.5%. On the other hand, the lead absorption signal

increased 8.0% after running the samples having the acid with the non-pyrolytic tube.

4. Nitric acid increases the suppression caused by sodium nitrate on the lead absorption signal and the hydrochloric acid increases the suppression caused by sodium chloride. Since each acid has a common anion with the corresponding salt, the pH of the solution appears to have a role on the extent of the interference process in highly acidic media.

5. The use of the lead absorption line at 217.0 nm compared to the line at 283.3 nm, results in better sensitivity in the presence of sodium chloride as an interferent.

6. The tube surface type has little effect on the molecular absorption spectra for either lead chloride or lead nitrate.

7. The molecular absorption spectrum of lead chloride results in three distinct peaks. Only the first of the three peaks can be correlated with lead chloride molecular absorption spectrum.

8. Although the second and third peaks do not appear to be typical molecular absorption spectra they do show a definite concentration correlation.

9. The lead nitrate absorption spectrum is a relatively flat continuum.

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