

# Matrix Interferences in Furnace Atomic Absorption Spectrometry

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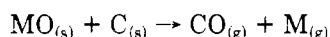
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**The extent of the interference of various concentrations of NaCl, NaClO<sub>4</sub>, and NH<sub>4</sub>Cl on the atomic absorption signals for Cd, Cr, Cu, and Pb has been determined for two microfurnace electrothermal atomizers (Varian cup and tube) and for a constant temperature furnace (Woodruff). Matrix concentrations of up to 10 mg/mL caused less than 5% signal suppression for the constant temperature Woodruff furnace while signal suppressions of up to 80% were observed for the other atomizers.**

Furnace atomizers have been used in atomic spectroscopy since the first decade of this century (1). The first application of a graphite furnace in a quantitative AAS determination was reported by L'vov (2-4). The developmental work of Massman (5), Woodruff (6-8), West and Williams (9), and Amos et al. (10, 11) has also helped to promote the use of this technique.

Furnace atomizers offer the advantage of separating the desolvation, decomposition, and atomization processes which precede the measurement of the atomic absorption signal into three distinct steps. If each of these processes can be fully accomplished before proceeding with the next, the matrix interferences which occur in flame atomization techniques could not be a problem. However, in practice, the atomization efficiency varies with the composition of the matrix and the graphite furnace is not interference free.

Campbell and Ottaway (12) have proposed a mechanism for the production of atoms in graphite atomizers based on the reaction



where M is the metal being atomized. The lowest temperature at which an atomic absorption signal could be measured (the appearance temperature) has been shown to correlate with the temperature at which  $\Delta G$  for this reaction becomes negative. Aggett and Sprott (13) and Fuller (14, 15) have also reported mechanistic studies but in these studies essentially ideal solutions of single metal analysis dissolved in dilute nitric acid were employed. As a result, these mechanistic studies cannot be directly extrapolated to the analysis of real analytical samples where the matrix is often complex with components of both lower and higher volatility and thermal stability than the analyte.

Matrix interferences can be classified into three groups: spectral, chemical, and physical interferences. Spectral interferences that are not caused by an overlap of atomic lines can be eliminated in most instances by using the background correction technique suggested by Koirtyohann and Pickett (16-18). Chemical interferences may be caused by reaction either on the surface of the graphite atomizer or in the vapor above the atomizer. Carbides of Ba, La, Zr, Ti, Nb, W, etc. are the only compounds that are stable in a graphite atomizer. A gas phase reaction interference mechanism has been proposed by West et al. (19-22) and by Matousek (23, 24).

Physical interferences may be caused by either occlusion of the analyte in the matrix, which has been proposed by Smeyers-Verbeke et al. (25), Cruz and Van Loon (26) and Churella and Copeland (27), or co-volatilization of the analyte along with a more volatile matrix as proposed by Hutton et al. (28). There is little agreement as to the primary causes of matrix interference in nonflame atomization. Some of the variation in the results may be due to the use of different atomizer designs by the various groups. The results obtained on the smallest commercially available atomizers (Varian graphite tube and cup) and the results obtained on the much larger Woodruff furnace atomizer represent extremes which may be extrapolated to estimate variations caused by furnace design. By measuring AAS signals of a few representative elements in matrices of varying concentrations and of varying thermal stability, a mechanism may be elucidated that will be more consistent with the results obtained by the other groups.

## EXPERIMENTAL

**Instrumentation.** Atomic absorption signals were measured on two spectrometer systems. The principal difference between the two systems is that the atom cell for one is a carbon rod atomizer (CRA) and the other is a Woodruff furnace. The first system consists of a Varian Techtron AA-6 Atomic Absorption Spectrometer with a BC-6 Background Correction Module, a M-63 Carbon Rod Atomizer, and a Varian Aerograph model A-25 recorder. The CRA was used with both the graphite tube and the graphite cup. Both of these atomizers are coated with pyrolytic graphite by the manufacturer and were used as received.

The second spectrometer system was a lab-built system consisting of a Woodruff furnace atomizer (Frontier Products), an EU-700 monochromator with a filter attachment (GCA/McPherson), an EU-701-30 photomultiplier tube housing and power supply (GCA/McPherson), a lab-built background corrected absorbance module, a high voltage power supply for lamp operation (Northeast Scientific Corp.), a half aluminized silica beam splitter (Corion Instrument Corp.), and a Linear model 285 two-pen recorder. The Woodruff furnace atomizer was resistance heated using a variable transformer rated for 220 V at 28 A (Superior Electric Co.) and a step-down transformer (General Electric Co.) which yielded 10 V ac at greater than 300 A. The graphite heater tubes of the furnace were 0.3650-in. (9.271-mm) o.d., 0.2055-in. (5.220-mm) i.d., and 5<sup>7</sup>/<sub>8</sub> in. (150 mm) long. The sample solutions were placed in graphite cups (4-mm i.d. and 7 mm deep), dried on a hot plate, and screwed onto the end of a threaded rod (1/8-in. diameter). The cup was then inserted into the preheated interior of the furnace where a gas-tight seal was formed between the cup and the seat on the support tube.

The background corrected absorbance module was constructed using the circuit diagrams of Donnelly, Eccleston, and Gully (29) with the following modifications. A 741 op-amp was used in place of the transistor pre-amp; a 755N log amp (Analog Devices, Inc.) was used in place of the log circuit. Two 556 multivibrators were used as the pulse generator in place of the 7474 flip-flop. An analog integrator was added to the module after construction was completed.

Single element hollow cathode lamps were used with both systems (Varian, Jarrell-Ash, Tekmar, and Cathodion) and a H<sub>2</sub> lamp in a hollow cathode design (Varian) was used as the continuum source for background correction.

**Solutions.** Stock solutions of 100 µg/mL of each of the metals studied were prepared from reagent grade metals for Se, Pb, Cd,

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Table I. Detection Limits, pg

element	wavelength	Woodruff furnace	CRA
As	193.7	25	180*
Cd	228.8	0.18	1.4
Cu	324.8	29	14
Pb	217.0	5	16
Sb	217.6	25	55*
Se	196.0	45	95*

Cu, and Zn and from  $\text{As}_2\text{O}_3$  for As and  $\text{SbCl}_3$  for Sb. Nitric acid was used to dissolve the metals. The final nitric acid concentration was 2–5%.  $\text{SbCl}_3$  was dissolved in HCl and  $\text{As}_2\text{O}_3$  was dissolved in a minimum amount of 30% NaOH.

Individual solutions were prepared by diluting appropriate amounts of the 1000  $\mu\text{g/mL}$  stock solutions using "class A" volumetric glassware that was soaked in 35%  $\text{HNO}_3$  overnight before use. All working solutions were stabilized by making them 1% in  $\text{HNO}_3$  and were analyzed within 24 h of preparation.

All the salts that were added as matrices were reagent grade and were used without further purification. The water used was deionized, distilled, and deionized again. The resistance was at least 2 M $\Omega$ .

**Procedure.** Both the Varian "mini-furnace" and the Varian cup atomizers were used following the manufacturer's operating instructions. Sample volumes of 5  $\mu\text{L}$  were dispensed by an Excalibur "Autopette" micropipet, and the solvent was evaporated at the highest voltage setting (0–10 in arbitrary units) at which the sample dried (in a period of ca. 20–25 s) without sputtering. The ash settings were adjusted as necessary for each analysis.

The samples were atomized at the lowest temperature which gave the maximum signal. Nitrogen was used as the purge gas for the Varian CRA tube and cup.

The Woodruff furnace was preheated to the desired temperature which was measured with a Pyro Micro-Optical Pyrometer (The Pyrometer Instrument Co., Inc.). The pyrometer was focused on the region of the furnace that is occupied by the sample cup. Samples were dispensed into graphite sample cups and the solvent was evaporated by heating the sample cup on a hot plate. The solvent evaporated in ca. 30 to 60 s without sputtering. The samples were dispensed with either a fixed volume micropipet (20  $\mu\text{L}$ , Oxford Laboratories) or a variable volume micropipet (1–20  $\mu\text{L}$ , Gilson Pipetman). Argon was used as the purge gas.

Except where noted, all measurements were made in the background corrected absorbance (BCA) mode.

**Pyrolytic Coating.** The interior of the Woodruff furnace was coated with pyrolytic graphite by flowing a 9:1 mixture of argon and propane through the furnace at 450 mL/min at 1100  $^{\circ}\text{C}$  for ca. 1 h.

## RESULTS AND DISCUSSION

Solutions were analyzed which were 0–1.5  $\mu\text{g Pb/mL}$  using the Woodruff furnace and the lab-built BCA module to determine if the lab-built system was operating properly. A linear regression analysis was performed on the plotted peak heights and peak areas. The calculated correlation coefficients were  $r = 0.9905$  and  $r = 0.9995$ , respectively.

The detection limits obtained for six representative metals using the Woodruff furnace system are listed in Table I along with values for the CRA system which were either measured or calculated (marked \*) from data in the CRA applications manual (30). These values were obtained using the equations presented by Skogerboe and Grant (31). The  $t$  statistic for the appropriate number of measurements and for the 95% confidence level was used for the estimate given. It may be noted that the Woodruff furnace system is 2–14 times better than the CRA system for all the elements presented except Cu. The Cu value is higher because the furnace temperature could not be raised above 2100  $^{\circ}\text{C}$  (the optimum temperature for Cu is 2200–2400  $^{\circ}\text{C}$  (32)).

Precision for both instruments was ca. 1–3% relative standard deviation (RSD) for determinations made by

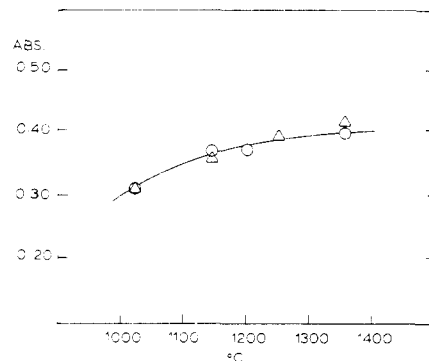


Figure 1. Absorbance vs. temperature for Pb. (O) 0.05  $\mu\text{g Pb/mL}$ , ( $\Delta$ ) 0.05  $\mu\text{g Pb/mL}$  in 10 000  $\mu\text{g NaClO}_4/\text{mL}$

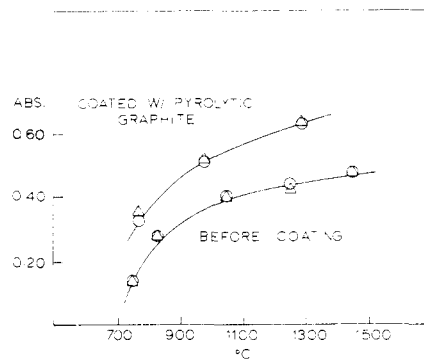


Figure 2. Absorbance vs. temperature for Cd. (O) 0.50  $\mu\text{g Cd/mL}$ , ( $\Delta$ ) 0.50  $\mu\text{g Cd/mL}$  in 10 000  $\mu\text{g NaClO}_4/\text{mL}$

measuring peak heights. Precision for determinations made by measuring the area under the recorded curves using the Woodruff furnace was ca. 5–8% RSD. Areas were not measured under the curves obtained with the CRA tube and cup. The relative standard deviations for the area measurements are larger because the height of the peak is a function of the rate at which the atoms enter (or are formed in) the optical path in the atom cell while the area under the peak is a function of the rate at which the atoms leave the optical path in the atom cell (14, 15, 33, 34). During the atomization of a sample using the Woodruff furnace, the sample cup forms a press-fit seal with the preheated interior of the furnace and the atoms formed are transported via diffusion down the heater tubes to either end (32). The time required for the signal to reach the maximum is ca. 1–5 s, depending on the temperature, and the time required for the signal to return to the base line is ca. 20–30 times longer. Therefore if a slow flow of argon is leaking past the cup-guard tube seal, it will affect the rate at which the atomic vapor diffuses out of the furnace more than the rate at which the atomic vapor is formed.

Solutions of lead and cadmium were analyzed using the Woodruff furnace. Peak heights obtained for the analysis as a function of temperature are shown in Figures 1 and 2, respectively. These plots are presented here to show the general trend of increasing signal (peak height) with increasing temperature. This functionality should be obtained for all elements if the time constant of the system is adequate. In the event that the time constant of the system is too long, a maximum signal will be measured (especially for the more volatile elements) at some temperature above which the atoms are entering and leaving the atom cell before the complete signal can be recorded. If the time constant is shorter, this maximum is not observed and the signal will remain fairly constant as the temperature is increased further (35). The time constant must be long enough, however, to remove any high frequency noise components from the signal.

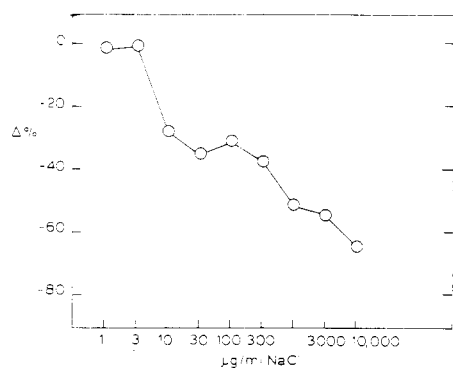


Figure 3.  $\Delta\%$  vs. NaCl concentration for Pb analysis with the CRA cup

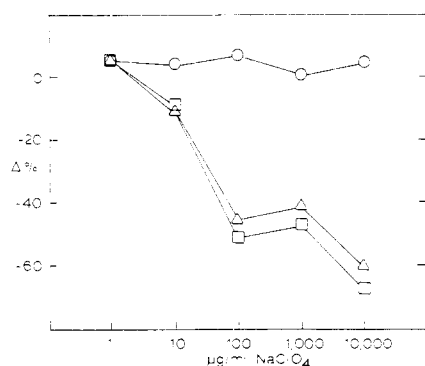


Figure 4.  $\Delta\%$  vs.  $\text{NaClO}_4$  concentration for Pb analysis. (O) Woodruff furnace, ( $\Delta$ ) CRA tube, ( $\square$ ) CRA cup

The results obtained for a Cd analysis using the Woodruff furnace after the interior had been coated with pyrolytic graphite are also shown in Figure 2. The increase in signal relative to the results obtained with an uncoated furnace demonstrates that the diffusion of the atoms through the graphite joints and, to a lesser extent, the graphite walls has been lessened by the pyrolytic coating.

Solutions containing  $0.50 \mu\text{g Pb/mL}$  and  $0.50 \mu\text{g Pb/mL}$  with  $1\text{--}10,000 \mu\text{g NaCl/mL}$  were analyzed using the Woodruff furnace with the monochromator set at the  $261.4\text{-nm}$  Pb line. A linear increase in signal with increasing NaCl concentration was measured. This dependence was not observed at either of the two more sensitive Pb lines,  $217.0 \text{ nm}$  and  $283.3 \text{ nm}$ , and no significant background absorbance was measured using the  $\text{H}_2$  lamp. It was therefore concluded that the interference was not due to scattering which would increase at shorter wavelengths and not due to molecular absorbance but must be caused by an overlap of atomic lines. This interference was attributed to the K contamination in the NaCl ( $40 \text{ ppm K}$ ) due to a K line at  $261.41 \text{ nm}$  overlapping the Pb line at  $261.4178 \text{ nm}$  (36). Solutions of KCl were successfully analyzed using the Pb lamp confirming the cause of the interference.

The  $261.4\text{-nm}$  line was chosen for the above analysis because the standard curve obtained with this line is approximately 40 times less sensitive than with the  $217.0\text{-nm}$  line. This allowed the use of solutions that were more concentrated and less subject to contamination from the water and acids used. Another source of contamination is due to the fact that the sample cups used with the Woodruff furnace adsorb a sufficient quantity of lead particulates from the laboratory air between analyses ( $\sim 1 \text{ minute}$ ) to give a full-scale response ( $1.0 \text{ au}$ ) at the  $217.0\text{-nm}$  line. Although the  $261.4\text{-nm}$  line is more convenient, its use was precluded by the K interference.

The same  $0.50 \mu\text{g Pb/mL}$  solutions as above were analyzed using the CRA cup using the  $217.0\text{-nm}$  line and the results are shown in Figure 3. The decrease in signal with increasing NaCl concentration is similar to the matrix interference effect

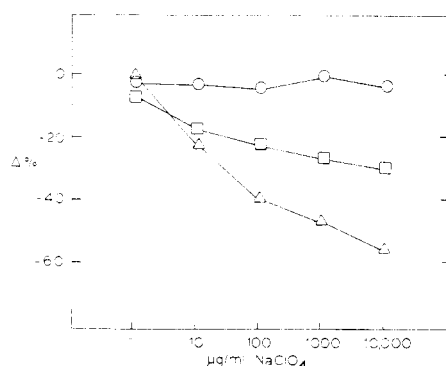


Figure 5.  $\Delta\%$  vs.  $\text{NaClO}_4$  concentration for Cd analysis. Legend as for Figure 5

Table II. Analysis of  $1.0 \mu\text{g Cu/mL}$  Solutions with Added Matrix Using the Woodruff Furnace (WF) at  $324.75 \mu\text{m}$  and the CRA Cup from Churella and Copeland (27)

Matrix	$\Delta\%$	
	WF	CRA
$5000 \mu\text{g NaCl/mL}$	+2	-40
$5000 \mu\text{g KCl/mL}$	-4	-40
$5000 \mu\text{g LiCl/mL}$	-4	-25
$5000 \mu\text{g NaClO}_4/\text{mL}$	+4	-15
$5000 \mu\text{g MgCl}_2/\text{mL}$	-3	-40

Table III. Analysis of  $0.50 \mu\text{g Cu/mL}$  with Added  $\text{NaClO}_4$  Using the Varian Atomizers ( $324.75 \text{ nm}$ )

$\mu\text{g NaClO}_4/\text{mL}$	atomizer	$\Delta\%$	
		low <sup>a</sup>	high <sup>a</sup>
1 000	cup	-21	-45
3 000		-38	-32
10 000		-59	-29
1 000	tube	-40	-76
3 000		-37	-52
10 000		-58	-47

<sup>a</sup> Ash setting: low  $\approx 500^\circ\text{C}$ ; high  $\approx 800^\circ\text{C}$  (27, 30).

that NaCl has on Cu (27). Solutions containing  $0.050 \mu\text{g Pb/mL}$  and  $0.050 \mu\text{g Pb/mL}$  plus  $1\text{--}10,000 \mu\text{g NaClO}_4/\text{mL}$  were analyzed using the Woodruff furnace and the CRA tube and cup; the results are shown in Figure 4. Similar solutions containing  $0.50 \mu\text{g Cd/mL}$  were analyzed using the Woodruff furnace with the  $326.1\text{-nm}$  line and solutions containing  $0.050 \mu\text{g Cd/mL}$  were analyzed using the CRA tube and cup using the  $228.8\text{-nm}$  line; the results are shown in Figure 5. (The reason for using different lines in the two systems is because of the high sensitivity obtained with the Woodruff furnace.) Contamination of the graphite cups by Cd particulates in the laboratory air was a problem and working at the less sensitive ( $\sim 450$  times) line was more convenient. The results are presented relative to the distilled water standards;  $\Delta\%$  was calculated by

$$\Delta\% = \frac{A_{\text{sm}} - A_s}{A_s} \times 100$$

where  $A_{\text{sm}}$  is the absorbance obtained for the standard with added matrix and  $A_s$  is the absorbance obtained for the standard without added matrix. The results obtained with the Woodruff furnace varied within experimental error while the signals obtained with the Varian tube and cup atomizers decreased with increasing  $\text{NaClO}_4$  concentration.

Solutions containing  $1.0 \mu\text{g Cu/mL}$  and  $1.0 \mu\text{g Cu/mL}$  plus  $5000 \mu\text{g matrix/mL}$  were analyzed using the Woodruff furnace. The results are presented in Table II along with the best results obtained on the CRA cup by Churella (27). Solutions

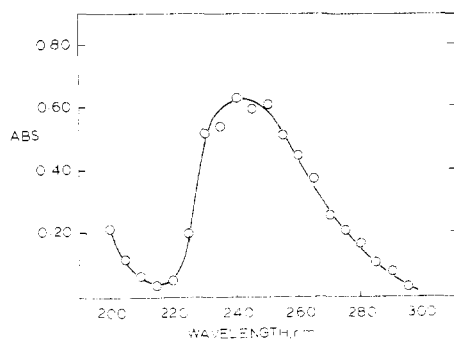


Figure 6.  $\text{NaClO}_4$  background spectrum

containing  $0.50 \mu\text{g Cu/mL}$  and  $0.50 \mu\text{g Cu/mL}$  plus  $1000\text{--}10000 \mu\text{g NaClO}_4/\text{mL}$  were analyzed using the Varian atomizers and the results are listed in Table III.

Only peak height data are presented because the peak areas followed the same trends as the peak heights and, with the larger uncertainty in the peak area measurements, there is no advantage in measuring areas. This conclusion is supported by other workers (25, 27).

These results (Figures 3–5 and Tables II and III) indicate that the Woodriff furnace atomizer is not plagued by the interferences found in the Varian atomizers and other graphite atomizers (19–28, 37). Therefore, the interference mechanism must be dependent on the length of the furnace tube because this is the principal difference between the Woodriff furnace atomizer and the other atomizer designs. The CRA tube and cup hold the sample contained in the graphite cup. The Woodriff furnace design offers the advantage of separating the atom cell from the sample container. The formation of the atomic vapor in the CRA tube and cup is kinetically limited by the rapid expansion of the gases filling the atomizers when the temperature of the graphite is increased from ca.  $500$  to  $1000\text{--}3000^\circ\text{C}$  in less than  $1.5$  s. The sample could be carried out of the atomizer during the expansion and the atomic vapor formation efficiency would be greatly affected. The samples analyzed using the Woodriff furnace experience the same rapid temperature increase in a graphite container. However, because the sample container and atom cell are separate and because the sample gases expand into the atom cell, the sample cannot leave the atom cell before complete atomization.

Solutions containing  $0.050 \mu\text{g Pb/mL}$  and  $0.050 \mu\text{g Pb/mL}$  with  $10000 \mu\text{g NaClO}_4/\text{mL}$  and  $0.50 \mu\text{g Cd/mL}$  and  $0.50 \mu\text{g Cd/mL}$  with  $10000 \mu\text{g NaClO}_4/\text{mL}$  were analyzed at temperatures between  $1025$  and  $1355^\circ\text{C}$  for Pb and  $750$  and  $1450^\circ\text{C}$  for Cd using the Woodriff furnace. The results obtained by measuring peak heights are presented in Figures 1 and 2, respectively. The rate at which the free atoms are formed increases with increasing temperature as discussed above but this rate is not affected by the presence of the  $20000\text{-fold}$  excess of a  $\text{NaClO}_4$  matrix. This would indicate that a vapor phase reaction which depletes the free atom concentration is not observed in the Woodriff furnace. It can be conjectured that a vapor phase reaction interference may be more pronounced at lower temperatures because of the greater stability of the compounds that could form in the vapor phase at these lower temperatures. However, as indicated in Figures 1 and 2, the presence of the matrix does not change the recorded signals by more than the standard deviation of the method.

A spectrum of the material present in the vapor phase in the Woodriff furnace when  $\text{NaClO}_4$  is added was recorded by placing  $10 \mu\text{g}$  of  $\text{NaClO}_4$  into the furnace at  $1250^\circ\text{C}$  and incrementing the monochromator over the  $200\text{--}295$  nm region. The spectrum obtained is presented in Figure 6; each point is an average of three determinations. This spectrum is very similar to the vapor phase  $\text{NaCl}$  spectrum (38) and an oxygen

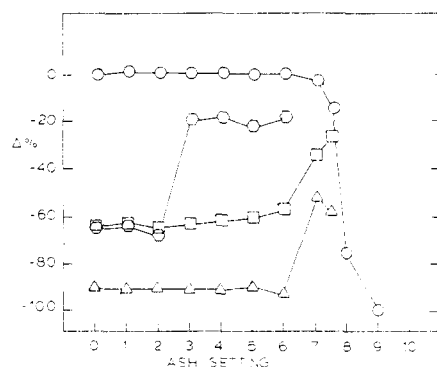


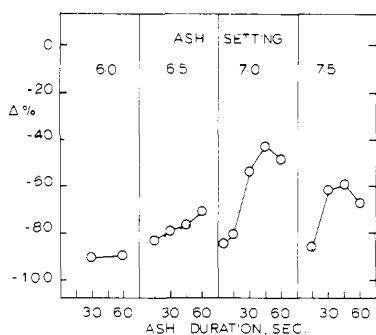
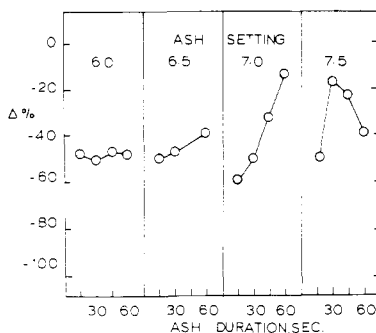
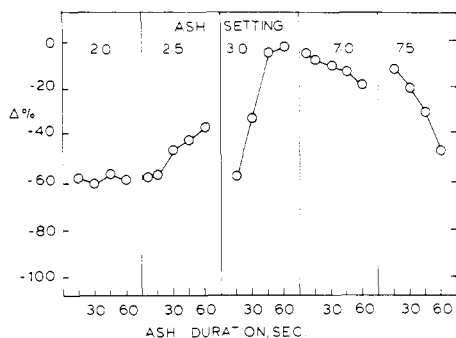
Figure 7.  $\Delta\%$  vs. ash setting. (O)  $0.050 \mu\text{g Cu/mL}$ , ( $\Delta$ )  $0.050 \mu\text{g Cu/mL}$  in  $10000 \mu\text{g NaCl/mL}$ , ( $\square$ )  $0.050 \mu\text{g Cu/mL}$  in  $10000 \mu\text{g NaClO}_4/\text{mL}$ , ( $\diamond$ )  $0.050 \mu\text{g Cu/mL}$  in  $10000 \mu\text{g NH}_4\text{Cl/mL}$

absorption has been observed by Churella in the CRA cup (27). Therefore, because  $\text{NaClO}_4$  is well known to be thermally unstable ( $\text{NaClO}_4 \rightarrow \text{NaCl} + 2\text{O}_2$ ) and the presence of  $\text{NaCl}$  and  $\text{O}_2$  have been confirmed, the formation of either a lead or cadmium chloride (or oxide) compound would seem possible. Matousek (23, 24) has postulated that the formation of a metal chloride in the vapor phase is responsible for the depressed signals measured when a chlorine-containing matrix is analyzed. The interference mechanism proposed by Matousek was based on results obtained with a CRA tube in which the atomic vapor is surrounded by the hot graphite walls as in the Woodriff furnace. It was shown (23, 24) that the signals are depressed only when the analyte and matrix are vaporized simultaneously as in the Woodriff furnace. If there is a vapor phase interaction between the free metal and other atoms in the atomizer, similar results should be observed in both. Because there is no change in the signal when the chlorine-containing matrix is added, it may be stated that a vapor phase reaction interference mechanism is probably not the major cause for the decrease in signal observed in the Varian atomizers.

A  $0.50 \mu\text{g Cu/mL}$  solution and  $0.50 \mu\text{g Cu/mL}$  solutions with  $10000 \mu\text{g/mL}$  of  $\text{NaCl}$ ,  $\text{NaClO}_4$ , or  $\text{NH}_4\text{Cl}$  added matrix (each added individually) were analyzed using the CRA cup and the results are presented as a function of ash setting in Figure 7. As indicated in this plot, the Cu signal (peak height) remains fairly constant (within experimental error) until a setting of "7" ( $\sim 800^\circ\text{C}$ ) is exceeded. Above this setting, the cup is hot enough to slowly vaporize the Cu during the ash stage and the amount of Cu remaining to be vaporized during the atomize stage is reduced. In the presence of  $10000 \mu\text{g NaCl/mL}$  added matrix, 90% of the signal is lost when ash settings up to "6" ( $\sim 600^\circ\text{C}$ ) are used. At a setting of "7", the signal is partially restored so that only ca. 55% is lost. At this setting, the cup is heated to approximately the melting point of  $\text{NaCl}$  ( $801^\circ\text{C}$ ). The resulting phase change alters the structure of the matrix and increases the efficiency of the atomization.

In the presence of  $\text{NaClO}_4$  and  $\text{NH}_4\text{Cl}$  matrices, ca. 65% of the Cu signal is lost at lower settings. The signals can be improved by raising the ash temperatures; at a setting of "3" the  $\text{NH}_4\text{Cl}$  interference can be lessened and at a setting of "7–7.5" the  $\text{NaClO}_4$  interference can be lessened. These improvements at the particular settings can be linked to the thermal stability of the matrices.  $\text{NH}_4\text{Cl}$  sublimates at  $340^\circ\text{C}$  and  $\text{NaClO}_4$  decomposes at  $482^\circ\text{C}$  to form  $\text{NaCl}$  which in turn will melt at  $801^\circ\text{C}$ .

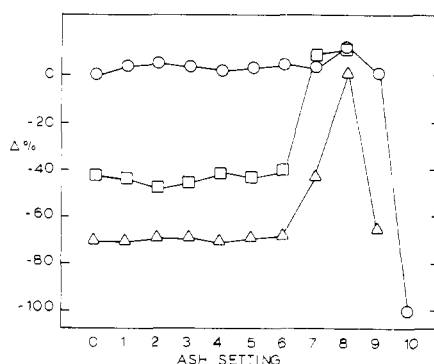
The effect that ash temperature has on the Cu signal was further studied by varying the ash time (5–60 s) for the analyses in the presence of the same matrices,  $\text{NaCl}$ ,  $\text{NaClO}_4$ , and  $\text{NH}_4\text{Cl}$ . The results are presented in Figures 8–10, respectively. By varying the ash temperature and the duration,

Figure 8.  $\Delta\%$  vs. ash duration, Cu in NaClFigure 9.  $\Delta\%$  vs. ash duration, Cu in  $\text{NaClO}_4$ Figure 10.  $\Delta\%$  vs. ash duration, Cu in  $\text{NH}_4\text{Cl}$ 

an optimum setting can be obtained. However, only the  $\text{NH}_4\text{Cl}$  matrix interference could be completely eliminated by using this method. The Cu signals recorded in the presence of NaCl and  $\text{NaClO}_4$  are still ca. 45% and 15% depressed at the best settings. The  $\text{NH}_4\text{Cl}$  interference can be eliminated because the matrix can be completely removed by sublimation while the signals obtained with the other two matrices present can only be partially improved without loss of Cu during the ash stage.

This experiment was repeated, replacing Cu with Cr at a concentration of  $0.50 \mu\text{g/mL}$  and the results are shown in Figure 11. The Cr signal did not decrease until an ash temperature of  $\sim 1950^\circ\text{C}$  (setting 10) was used. The addition of  $10000 \mu\text{g/mL}$  concentrations of NaCl and  $\text{NaClO}_4$  yielded depressed signals for Cr as for Cu. These signals were improved by adjusting the ash settings to "8" ( $\sim 1150^\circ\text{C}$ ) for 15 s for  $\text{NaClO}_4$ . These settings are adequate for the sufficient alteration of the physical state of the matrix to preclude an interference. The NaCl residue from both sources will be completely melted and sufficiently vaporized at these settings so that the Cr will not be surrounded or trapped by the matrix and the efficiency of the atomization will be improved without loss of Cr during the ash stage.

These results (Figures 7–11) indicate that a co-volatilization interference mechanism is not the predominant cause of the depressed signals contrary to the conclusions drawn by Ottaway et al. (28). If co-volatilization were the predominant

Figure 11.  $\Delta\%$  vs. ash setting, Cr analysis, CRA cup. (O)  $0.050 \mu\text{g Cr/mL}$ , (□)  $0.050 \mu\text{g Cr/mL}$  in  $10000 \mu\text{g NaClO}_4/\text{mL}$ , (Δ)  $0.050 \mu\text{g Cr/mL}$  in  $10000 \mu\text{g NaCl/mL}$ Table IV. Signal Depression for  $10^{-10}$  mol Cu in a NaCl Matrix

matrix crystal size, mol	$\Delta\%$
$10^{-9}$ – $10^{-8}$	–60
$10^{-10}$ – $10^{-9}$	–20
$10^{-11}$ – $10^{-10}$	–5
$10^{-12}$ – $10^{-11}$	0

cause, the signals should decrease at higher temperatures as more of the analyte is vaporized along with the matrix. The signal should be better at lower settings and not at the higher settings as shown by these results.

Churella and Copeland (27) have studied the effect that ash temperature has on the "crystal" size of the residue present at the end of the ash stage and the signals that follow. They have shown via scanning electron micrographs that the magnitude of the interference is related to the size of the crystals for NaCl and  $\text{NaClO}_4$  matrices; larger crystals result in greater signal depressions. When the crystals are small and the sample residue is dispersed over the floor of the atomizer instead of being in large localized crystals, the signals are less depressed. If the crystals can be completely broken up into very small particles which are evenly distributed in the atomizer, the signals will be restored to the distilled water standard values. The addition of viscous acids ( $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ ) or an unstable reagent ( $\text{Na}_2\text{O}_2$ ) that will decompose and release a gas can be used to break up the dried residue during the ash stage. Also the addition of  $\text{HNO}_3$  will lessen the depression because of the formation of less stable compounds, i.e.,  $\text{NaNO}_3$  and HCl. The results of these workers (27) support the conclusions that can be drawn from this work. Namely, co-volatilization and vapor phase reactions are not major causes of matrix interferences and occlusion of the analyte in the inorganic matrix crystals is implicated as a major mechanism.

The shortest distance that a matrix crystal that has occluded the analyte must travel to escape the atomizer without a collision with the walls of the atomizer is 9 mm for the CRA cup, 5 mm for the CRA tube, and 150 mm for the Woodriff furnace. It is possible for a matrix crystal to be carried out of the CRA atomizers as the temperature of the atomizer increases from  $\sim 500$  to  $2500^\circ\text{C}$  in less than 1.5 s without complete vaporization of a large crystal. As the temperature increases, the gases that fill the CRA tube and cup are expanding to ca. four times the original volume occupied at  $500^\circ\text{C}$  and the gases will rapidly flow out of the atomizer as the expansion occurs. The volume of the tube portion of the Woodriff furnace is 67 times the volume of the sample cup. As the temperature of the sample cup increases, the gases will expand into the Woodriff furnace and carry the sample crystals into the preheated furnace atom cell and not out of

Table V. NBS Orchard Leaves Analysis

element	wave-length, nm	concentration, ppm		
		Woodriff furnace	CRA cup	certified
Pb	205.3	46 ± 2	<1	45 ± 3
Zn	307.6	29 ± 1	<4	25 ± 3
Cu	324.8	---	11 ± 1	12 ± 1

the atom cell as in the Varian atomizers.

A semi-quantitative correlation between the size of the matrix crystals and the magnitude of the signal depression can be drawn by studying the scanning electron micrographs of Churella and Copeland (27). Listed in Table IV is the approximate number of moles of matrix in the largest crystals found in the CRA cup at the end of the ash cycle. These numbers were calculated assuming a crystal thickness of 0.1 to 1  $\mu\text{m}$ . The total amount of analyte was  $10^{-10}$  mol.

Considering that the gases in the CRA atomizers are expanding to four times the original volume during the atomize stage, a large crystal of matrix could be carried out of the atomizer as the surface of the crystal vaporizes and the matrix vapor produced travels along with the rapidly expanding inert gas. It is conceivable that a large fraction of the analyte atoms (more than 50%) could be occluded in the matrix when the signal is depressed by 60%. The analyte would not be reduced to the free metal because it is trapped in the matrix. When the maximum crystal size of the matrix found at the end of the ash cycle can be decreased to one to two orders of magnitude smaller than the total amount of analyte ( $10^{-12}$  to  $10^{-11}$  mol of matrix per crystal and a total of  $10^{-10}$  mol of analyte) less than 10% of the analyte may be occluded and the analyte will not be lost along with the matrix. As stated above, the analyte that may be occluded in the matrix, when the sample is analyzed with the Woodriff furnace, will be carried into the preheated atom cell where there is sufficient time for the complete decomposition of the matrix to free the analyte.

To check the accuracy of the atomizers studied, a National Bureau of Standards orchard leaves sample (standard reference material 1571) was digested using a 2:1  $\text{HNO}_3\text{:HClO}_4$  mixture in a microwave oven for 30 min (39). The acid fumes were exhausted through a fume hood. The dry residue was dissolved in distilled deionized water and a few drops of HF were added to aid in the dissolution of a small insoluble portion of the residue which according to the certificate of analysis is a siliceous material. The solution was analyzed using the CRA cup and the Woodriff furnace; the results are listed in Table V. The result obtained for Pb and Zn with the Woodriff furnace and the result obtained for Cu with the CRA cup were tested with an *F*-test and no significant difference was found between these values and the certified values at the 0.01 level. The wavelengths chosen for Pb and Zn are not the most sensitive and were chosen because of the high concentrations of these elements in the diluted samples. The sample was not analyzed for Cu using the Woodriff furnace because the temperature needed for a valid Cu determination could not be attained with the transformer at the maximum setting. (This is probably due to oxidation of the transformer windings with prolonged use at greater than 5 kVA which results in a large energy loss in the transformer.) The results obtained with the CRA cup are acceptable for Cu only and the absorption signals measured for Pb and Zn were not significantly different from the random fluctuations in the base line. The matrix present in the CRA cup and the Woodriff furnace after the solvent has been evaporated is predominantly the undigested siliceous material found in the orchard leaves and the salts that were dissolved after the digestion. This matrix should be more thermally stable than

the very volatile metals Pb and Zn. It is conceivable that because the Cu determination was not affected by the matrix, an ash setting of  $\sim 800^\circ\text{C}$  is sufficient to alter the matrix and release the Cu to be reduced. Because Pb and Zn as metals and as metal chlorides are very volatile, the analyte would be lost during the ash stage if a temperature setting of  $800^\circ\text{C}$  were used and if a lower setting were used the matrix would not be sufficiently altered to release the analytes during the rapid atomization. The orchard leaves analysis and the Cr analysis (Figure 11) indicate that the CRA will yield reliable results only for very nonvolatile metals or when the matrix is of much greater volatility. When the matrix and the analyte are of similar volatilities, the results obtained for an analysis may be completely unreliable, as much as 90% low.

The major causes for matrix interference that have been postulated in the literature are either a physical loss of the analyte before the analyte-containing compound can be decomposed to produce the free metal or a chemical loss of the analyte through vapor phase reactions with the components of the sample matrix. It has been shown by this work that the physical loss of the analyte via co-volatilization of the analyte during the ash stage along with a more volatile matrix is not observed in the use of the CRA tube and cup. The chemical loss of the analyte through vapor phase reactions has not been observed even at temperatures which are  $200\text{--}300^\circ\text{C}$  lower than the normal atomization temperatures. However, the size of the crystalline residue remaining at the end of the ash stage does correlate with the magnitude of the signal depressions. The fact that the gases in the atomizer will expand very rapidly during the atomization of the residue does indicate that a large crystal which may contain a major fraction of the analyte atoms may be swept out of the atomizer by the rapid expansion before the atomization process is complete. Therefore, occlusion of the analyte in the inorganic matrix crystals must be a principal matrix interference mechanism. Furthermore, this interference mechanism is active only in the CRA tube and cup and the use of the Woodriff furnace is not hindered by the composition and resulting thermal stability of the inorganic matrix.

## LITERATURE CITED

- (1) A. S. King, *Astrophys. J.*, **27**, 353 (1908).
- (2) B. V. L'vov, *J. Eng. Phys.*, **2**(2), 44 (1959).
- (3) B. V. L'vov, *J. Eng. Phys.*, **2**(11), 56 (1959).
- (4) B. V. L'vov, *Spectrochim. Acta*, **17**, 761 (1961).
- (5) H. Massman, *Spectrochim. Acta, Part B*, **23**, 215 (1969).
- (6) R. Woodriff, R. W. Stone, and A. M. Held, *Appl. Spectrosc.*, **22**, 408 (1968).
- (7) R. Woodriff and G. Ramelow, *Spectrochim. Acta, Part B*, **23**, 665 (1968).
- (8) R. Woodriff and R. W. Stone, *Appl. Opt.*, **7**, 1337 (1968).
- (9) T. S. West and X. K. Williams, *Anal. Chim. Acta*, **45**, 27 (1969).
- (10) M. D. Amos, *Am. Lab.*, **2**(8), 33 (1970).
- (11) M. D. Amos, P. A. Bennett, K. G. Brodie, P. W. Y. Lung, and J. P. Matousek, *Anal. Chem.*, **43**, 211 (1971).
- (12) W. C. Campbell and J. M. Ottaway, *Talanta*, **21**, 837 (1974).
- (13) J. Aggett and A. J. Sprott, *Anal. Chim. Acta*, **72**, 49 (1974).
- (14) C. W. Fuller, *Analyst (London)*, **99**, 739 (1974).
- (15) C. W. Fuller, *Analyst (London)*, **100**, 229 (1975).
- (16) S. R. Koirtyohann and E. E. Pickett, *Anal. Chem.*, **38**, 1087 (1966).
- (17) S. R. Koirtyohann and E. E. Pickett, *Anal. Chem.*, **37**, 601 (1965).
- (18) S. R. Koirtyohann and E. E. Pickett, *Anal. Chem.*, **38**, 585 (1966).
- (19) K. W. Jackson and T. S. West, *Anal. Chim. Acta*, **59**, 187 (1972).
- (20) D. Alger, R. G. Anderson, I. S. Maines, and T. S. West, *Anal. Chim. Acta*, **57**, 271 (1971).
- (21) R. G. Anderson, I. S. Maines, and T. S. West, *Anal. Chim. Acta*, **51**, 355 (1970).
- (22) R. G. Anderson, H. N. Johnson, and T. S. West, *Anal. Chim. Acta*, **57**, 281 (1971).
- (23) J. P. Matousek, Federation of Analytical Chemistry and Spectroscopy Societies, 1976 Meeting, Philadelphia, Pa., Nov. 1976, Paper 306.
- (24) E. J. Czobik and J. P. Matousek, *Anal. Chem.*, **50**, 2 (1978).
- (25) J. Smeyers-Verbeke, Y. Michotte, P. Van den Winkel, and D. L. Massant, *Anal. Chem.*, **48**, 125 (1976).
- (26) R. B. Cruz and J. C. Van Loon, *Anal. Chim. Acta*, **72**, 231 (1974).
- (27) D. J. Churella and T. R. Copeland, *Anal. Chem.*, **50**, 309 (1978).
- (28) R. C. Hutton, J. M. Ottaway, and T. Platt, Federation of Analytical Chemistry and Spectroscopy Societies, 1976 Meeting, Philadelphia, Pa., Nov. 1976, Paper 307.
- (29) T. H. Donnelly, A. J. Eccleston, and R. J. Gully, *Appl. Spectrosc.*, **29**, 149 (1975).

- (30) B. R. Culver, "Analytical Methods for Carbon Rod Atomizers", Varian Techtron Pty. Ltd., Springdale, Victoria, Australia, 1975.  
 (31) R. K. Skogerboe and C. L. Grant, *Spectrosc. Lett.*, **3**, 215 (1970).  
 (32) R. Woodruff, Momir Marinkovic, R. A. Howard, and I. Elezer, *Anal. Chem.*, **49**, 2008 (1977).  
 (33) C. W. Fuller, *Proc. Anal. Div. Chem. Soc.*, **13**, 273 (1976).  
 (34) C. W. Fuller, *Analyst (London)*, **101**, 798 (1976).  
 (35) D. D. Siemer and R. W. Stone, *Appl. Spectrosc.*, **29**, 240 (1975).  
 (36) G. R. Harrison (Massachusetts Institute of Technology), "Wavelength Table

- of 100 000 Spectrum Lines", John Wiley and Sons, New York, 1939.  
 (37) B. V. L'vov, *Federation of Analytical Chemistry and Spectroscopy Societies*, 1976 Meeting, Philadelphia, Pa., Nov. 1976, Paper 214.  
 (38) B. R. Culver and T. Surles, *Anal. Chem.*, **47**, 920 (1975).  
 (39) P. Barrett, L. J. Davidowski, Jr., K. W. Penaro, and T. R. Copeland, *Anal. Chem.*, **50**, 1021 (1978).

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# Analysis of Coal Liquids by Mass-Analyzed Ion Kinetic Energy Spectrometry

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**Particular nitrogen-containing compounds, in some cases individual isomers, can be identified in coal liquid samples by mass-analyzed ion kinetic energy spectrometry (MIKES). This is done directly, without prior treatment or fractionation of the sample. Isobutane chemical ionization (CI) is employed to give an approximate molecular weight profile of the coal liquid. Nitrogen-containing ions are recognized by their enhanced tendency for charge stripping as evident in  $E/2$  mass spectra or by using ammonia as the CI reagent. In selected cases, comparison with authentic compounds has been used to verify the MIKES identifications.**

This paper represents an attempt to apply the powerful new method of mass-analyzed ion kinetic energy spectrometry (MIKES) (1, 2) to coal liquefaction products. The complexity of these samples (3), their growing practical importance (4), and the laboriousness of chromatographic analysis (5), all indicate the desirability of evaluating all available alternatives. MIKES is a nonchromatographic procedure in which individual components are mass-selected after ionization and then identified by mass analysis of their dissociation products. Qualitative identification of individual components in natural products, particularly plant tissue, has been achieved with minimal sample pretreatment (6, 7) and these successes have encouraged the present undertaking.

The complexity of coal liquids is such that it is desirable to confine attention to certain groups of constituents. Indeed, selectivity for particular functional groups must be seen as a decided advantage in any analytical technique. Such selectivity can be achieved in MIKES by controlled pyrolysis (8) or by use of selective ionization techniques, as in negative CI/MIKES (9). In the latter approach only compounds of interest are ionized. We have chosen to explore selective ionization as well as an alternative approach in which a general ionization method (isobutane chemical ionization) is employed. This is followed by mass analysis with functional group screening being done using a high energy reaction of the selected ion. The reaction we use, charge stripping, has an enhanced cross section for nitrogen-containing compounds and these can therefore be recognized. This is most efficiently done in the course of a single magnetic scan taken with an appropriate setting of the second analyzer. Since this electrostatic analyzer measures kinetic energy to charge ratio, doubly charged ions occur at one half the normal setting,  $E$ . From the resultant  $E/2$  mass spectrum (10), one can pinpoint

those ions likely to contain nitrogen. Each such ion can then be examined individually by means of its MIKES spectrum.

In addition to evaluating these approaches to functional group screening, we are concerned here with how readily individual compounds are identified by MIKES and with whether or not isomers can be distinguished. The use of a relatively soft ionization method (isobutane CI) should also provide a qualitative picture of the molecular weight distribution in the sample, as has been done using field ionization mass spectrometry (11).

## EXPERIMENTAL

The MIKES instrument has been described previously (12). The coal liquids sample was placed in a glass capillary ( $\sim 1 \mu\text{L}$ ) and introduced to the mass spectrometer source using a direct insertion probe. Chemical ionization was employed using isobutane as reagent gas at a pressure of approximately 0.3 Torr. Ammonia chemical ionization was done using an isobutane ammonia mixture (10:1) (13). MIKES spectra were typically taken at scan rates of  $1 \text{ amu s}^{-1}$ . They are reproducible to within a few percent relative abundance. The source pressure was monitored using a capacitance manometer (MKS Baratron type 221).  $E/2$  scanning was performed by first setting the magnet to pass an arbitrarily chosen ion which showed a relatively strong charge stripping peak in its MIKES spectrum. The electrostatic analyzer voltage was then optimized to allow detection of the charge stripping peak maximum. The actual analyzer voltage was slightly less than 50%  $E$  due to the endothermicity of charge stripping (10). The magnet could then be scanned and the  $E/2$  spectrum of the entire sample recorded.

The relative charge stripping abundances (Table I) were obtained at a constant collision gas pressure (indicated as  $5 \times 10^{-5}$  Torr, estimated as  $1-2 \times 10^{-3}$  Torr) in the second field free region. The reported values represent an average of three or more measurements.

Nitrogen bases were extracted from the coal liquids by the following simple procedure: 1 g of coal liquids was diluted with 15 mL of toluene and extracted first with 15 mL of aqueous 2 N HCl, then twice with 15 mL each of 6 N HCl. The aqueous layer was retained and neutralized with concentrated  $\text{NH}_4\text{OH}$  to pH 10. The basic mixture was then extracted with three 15-mL volumes of toluene. The toluene fraction was dried over anhydrous  $\text{MgSO}_4$  and then evaporated to minimal volume. Approximately 1  $\mu\text{L}$  of the resulting basic extract was analyzed.

The coal liquefaction sample was obtained from K. C. Chao, Purdue University, and is otherwise uncharacterized.

## RESULTS AND DISCUSSION

Figure 1 shows part of the isobutane CI mass spectrum of the coal liquid evaporated from a direct insertion probe at 90  $^\circ\text{C}$ . Only low abundance ions occurred at lower and higher