

Interference of Salt Matrices in the Determination of Copper by Atomic Absorption Spectrometry with Electrothermal Atomization

D. J. Churella¹ and T. R. Copeland*

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

This work examines the concentration dependent interferences of several alkali and alkaline earth halides in the atomic absorption spectrometric determination of copper using a carbon cup electrothermal atomizer. The unusual interference of NaClO_4 is also investigated. The addition of Na_2O_2 is shown to eliminate or substantially reduce the interferences caused by these salts both in pure solutions and in seawater. Occlusion of the analyte is proposed as the primary mechanism of these interferences.

When electrothermal (nonflame) atomization techniques were first being developed by L'vov, Massman, Amos, and others (1-5), it was a common opinion that, in contrast to flame methods, determinations could be made relatively free from interferences caused by the matrix. With the advent of commercial instrumentation and a mushrooming interest in the method, it was discovered that the signal obtained for a metal was very much a function of the matrix involved and many interferences were noted.

There is little general agreement among the authors of interference studies (6-11) as to the exact mechanism of interferences. West et al. (7) show that suppressions are due to gas-phase interactions between atomic species and condensing interferences, Aggett and Sprott (8) and Segar and Gonzalez (9) cite metal and compound volatility as the major consideration in interferences, and Cruz and Van Loon (10) and Smeyers-Verbeke et al. (11) support the occlusion hypothesis of interference. They all agree, however, that interferences are probably due to complex combinations of several factors.

In order to understand the mechanisms of interference, it is important to know something of the mechanism of atomization of the analyte. Campbell and Ottaway (12) proposed a mechanism based on the reduction of the metal atoms in the gaseous state. Appearance temperatures for several metals were shown to be in agreement with the lowest temperatures at which the carbon reduction reaction becomes thermodynamically feasible. Kinetic studies by Fuller (13, 14) showed that the most probable reaction mechanism involves a slow first-order reduction of metal oxide by carbon followed by rapid volatilization of the metal formed.

Comparison of these and other studies must be done with consideration for the equipment employed and the chemical composition of the matrix. Commercially available equipment differs greatly in the total mass of the atomizer and the power supplied to it. Consequently the rate of change of the drying, ashing, and atomizing temperatures varies widely. The rate of temperature elevation, final temperature of each cycle, and length of time the sample remains at the temperature maxima, all would be expected to affect the size and composition of the crystals formed from remnants of the matrix. Measurement of parameters such as appearance temperatures from standard solutions (12) is largely independent of the time

required to reach that temperature and reasonable agreement with thermodynamic calculations could be expected. However, calculations based on thermodynamics for atomizers (such as employed in this study) where temperature changes over 500 °C/s are common, are essentially meaningless.

Kinetic interpretations of matrix interferences must also be made with care. The kinetic studies of atomization processes carried out by Fuller (13, 14) indicate a slow first-order reduction of the metal oxide by the carbon atomizer followed by rapid vaporization of the metal formed. This rate would be significantly affected by the size of the matrix/carbon interface (crystal size) as well as the actual crystal composition. Thus, although thermodynamic and kinetic studies of atomization are valuable in predicting important parameters in the atomization process, they do not necessarily afford information predicting the causes and extent of matrix interferences.

Electrothermal atomization has several advantages over flame atomization including extremely small sample volume, improvements of up to 2-3 orders of magnitude in sensitivity, and the elimination of lengthy pretreatment for the destruction of organic matter (8). It is thus of particular use in biological analysis where one is often working with very small samples of tissue which contain trace amounts of the metal of interest.

Biological samples, by nature, contain rather large amounts of salts (e.g., 1000-3500 µg/mL NaCl and 1400-6300 µg/mL KH_2PO_4 in addition to others (15)) and these salts can have a distinct effect on the accuracy of an analysis. Also, in wet digestion of samples, it is common practice to add acids such as HNO_3 and HClO_4 to the sample. If these acids are not completely destroyed in the digestion process, they will be present during the analysis and could have an effect on the response of the analyte. It was the purpose of this study to determine what effect these salts would have on the analysis for copper and to perhaps shed some light on the poorly understood origin, nature, and extent of these interactions.

EXPERIMENTAL

Apparatus. All experiments were performed on a Varian-Techtron AA-6 Atomic Absorption Spectrophotometer equipped with a CRA-63 electrothermal atomizer, a BC-6 background corrector, and a Varian Aerograph model A-25 recorder. Jarrell-Ash and Varian single element hollow cathode lamps were used as light sources. Graphite cups were used in the atomizer and N_2 was employed as the sheath gas. The CRA-63 atomizer offers both step and ramp atomizer modes. The voltage step mode afforded larger more reproducible signals and was used exclusively in this study. The 324.75-nm copper resonance line was employed for all analyses using a spectral bandpass of 0.5 nm and a slit height of 10 mm.

Experiments were performed to determine whether significant differences in the degree of signal suppression would be found measuring peak heights rather than areas. For all solutions studied, peak heights and mechanically or electronically integrated areas showed identical % suppression within experimental error. Consequently, absorbances were determined by measuring peak heights. Peak heights were measured from the recorder traces rather than using the AA-6 peak mode as the former was found

¹ Present address, Polaroid Corp., Cambridge, Mass. 02139.

to be more reproducible. Thus the measurement time constant was primarily that of the recorder, measured to be 0.3 s full scale. The peak height mode of the AA-6 also exhibited % suppressions identical to the other measurement modes within their (larger) experimental error.

Samples were dispensed into the cup using a 5- μ L micropipet with disposable plastic tips.

Atomizer temperatures were measured using a model 95 Pyro Micro-optical pyrometer. The area of the cup where temperatures were measured was inside the cup just below the optical path representing a temperature intermediate between the floor of the cup and the temperature in the optical path.

Electron micrographs of the matrix residues in the atomizer cups were obtained using an AMR 1000 scanning electron microscope and Polaroid type 52 film.

Reagents. All chemicals used were reagent grade. Water was distilled and doubly deionized and had a minimum resistivity of 2.0 M Ω .

All volumetric glassware was cleaned in hot, concentrated nitric acid before first use and was soaked overnight in ~ 1 M nitric acid between uses. Glassware was marked and used exclusively for one metal.

Stock solutions, 1000 μ g/mL, of metals were prepared by dissolving 1.000 g of pure metal in a minimum amount of concentrated HNO₃ and diluting to 1 L. Solutions were stored in polyethylene bottles. Solutions of matrix compound, 20000 μ g/mL, were prepared as needed. Working solutions were freshly prepared before use by adding appropriate volumes of stock metal and salt by buret to 100-mL flasks and diluting to volume. Unless otherwise noted, all solutions contain 1.0 μ g/mL copper.

General Procedure. Nonspecific absorption of salt matrices was checked by running a sample of 20000 μ g/mL salt solution in total absorbance mode. If peak heights greater than 5 mm (2% of full scale) were obtained, the whole series was run in the background corrected mode.

In a given series, the pure metal solution was run first, then the metal plus salt solutions were run in order of increasing salt concentration. Since results are reported relative to the response of the pure metal solution, this solution was run periodically throughout the series and at the end of the series. If the response of the pure solution changed during the series because of cup deterioration, the other solutions were compared to the most recent run of the pure solution. At least three replicate samples of each solution were run for each set of conditions.

In the two-number system of notation used in this work to specify dry, ash, and atomize setting, the first number indicates the relative voltage and the second number is the time in seconds for the particular cycle as read from the CRA-63 power supply. The drying time was generally kept at 25 s and the drying voltage adjusted so that the sample just finished drying at the end of the cycle. Ash settings of 5/10 and 7.25/30 were used.

The low ash setting of 5/10 resulted in a final temperature of 350 to 400 $^{\circ}$ C. The high ash temperature reached 975 to 1050 $^{\circ}$ C depending on the condition of the cup and support rods. Unless otherwise noted, the atomize setting was 8/3 which resulted in a final temperature of 2500 $^{\circ}$ C. The cups were fired at least three times between sample injections to ensure that any residual matrix had been removed.

RESULTS AND DISCUSSION

Effect of Mineral Acids. Solutions were analyzed which were 1.0 μ g/mL in Cu and either 1.0 M or 0.001 M in various mineral acids. Solutions with these same concentrations of Cu and acids in addition to being 3000 μ g/mL NaCl were also run to determine the effect of these acids on the interference of NaCl. The results are shown in Table I.

The data are presented as $\Delta\%$ which is the amount the copper absorbance has changed in the presence of the interferent relative to the copper absorbance in a distilled water solution. It is calculated according to the equation:

$$\Delta\% = \frac{P_m - P_s}{P_s} \times 100 \quad (1)$$

where P_m is the peak height of the analyte in the presence of

Table I. Effect of Various Acids on NaCl Interference

Acid	Cu + acid, $\Delta\%$		Cu + acid + NaCl vs. Cu, $\Delta\%$		Cu + acid + NaCl vs. Cu + NaCl, $\Delta\%$	
	Low ash	High ash	Low ash	High ash	Low ash	High ash
NaCl only			-64	-26		
1 M HCl	-4	-3	-73	-40	-26	-19
0.001 M HCl	-1	-3	-65	-28	-4	-3
1 M HNO ₃	-1	-4	-26	-26	+104	0
0.001 M HNO ₃	-3	-6	-42	-18	+60	+11
1 M H ₂ SO ₄	-2	-5	-30	-29	+92	-4
0.001 M H ₂ SO ₄	-4	-2	-33	-26	+84	0
1 M HClO ₄	-55	-17	-96	-89	-88	-84
0.001 M HClO ₄	-4	-8	-66	-41	-8	-20
1 M H ₃ PO ₄	-31	-14	-21	-15	+119	+15
0.001 M H ₃ PO ₄	-7	-9	-56	-50	+22	-33
1 M CH ₃ COOH	-6	-13	-65	-46	-4	-27
0.001 M CH ₃ COOH	-8	-13	-67	-38	-8	-17

the matrix and P_s is the peak height of the standard solution. This method normalizes the data, overcoming slight day-to-day variations in the absolute absorbance of the standard solution, and makes possible the direct comparison of the effect of various matrices. Except for 1 M HClO₄ and H₃PO₄, the acids alone caused generally small changes in the Cu signal. High ash conditions resulted in a slightly greater loss in Cu signal than low ash. However, HClO₄ and H₃PO₄ caused marked reductions in the signal at low ash (-55% and -30.7%, respectively), with considerable improvement in high ash (-16.8% and -14.2%, respectively). The 0.001 M concentrations of these acids were consistent with the other acids in causing only small reductions in the signal.

These same acids in the presence of NaCl presented an entirely different picture. When compared to the peak height of the pure Cu solution (center two columns of Table I), these matrices caused a much more severe depression of the signal than with the acids alone in all cases except for 1 M H₃PO₄ at low ash.

When compared to the response of a solution containing only Cu + NaCl (right two columns), HNO₃, H₂SO₄, and H₃PO₄ caused an enhancement of the Cu signal. In other words, they suppressed the interference of NaCl. The most effective suppression of the NaCl interference was achieved with a 1 M concentration of these acids at low ash conditions. High ash conditions resulted in an enhancement of the signal in only two cases, 1 M H₃PO₄ and 0.001 M HNO₃. These results are in agreement with Matousek (16) who found that H₃PO₄ significantly reduced the interference of NaCl on Cu and Pb solutions.

Effect of Various Salts. Matrix solutions containing either 0.5 μ g/mL or 1.0 μ g/mL Cu and varying amounts of inorganic salts were also investigated. The interference trends for LiCl and NaCl (Figures 1 and 2) are the same, their curves being almost superimposable. There is no interference until about 300 μ g/mL salt, then a gradual increase in interference until at 10000 μ g/mL, about 80% of the Cu signal is lost. Using the high ash cycle decreases the interference and causes the $\Delta\%$ curve to drop off more gradually. The curves for KCl and KI are the same as for NaCl and are not included.

AlCl₃ (Figure 3) follows the same general trend as the above salts except that the curves drop off at considerably lower concentrations and tend to level off above 3000 μ g/mL salt.

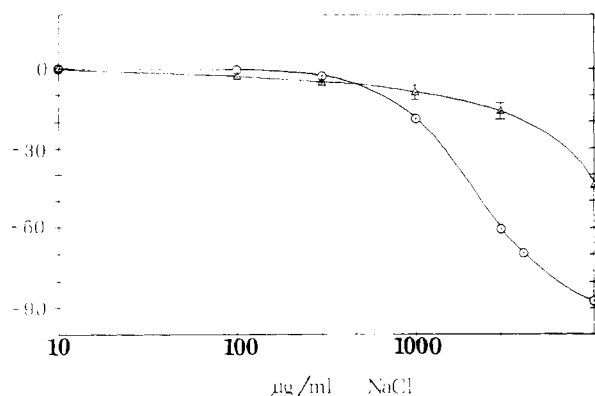


Figure 1. Effect of NaCl on Cu absorbances. 1 $\mu\text{g/mL}$ Cu, (Δ) high ash conditions, (O) low ash conditions

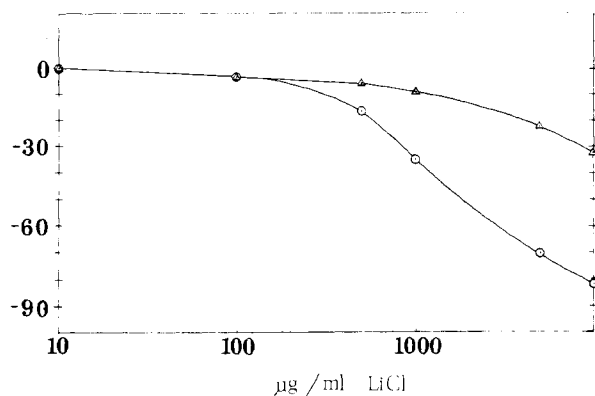


Figure 2. Effect of LiCl on Cu absorbances. 1 $\mu\text{g/mL}$ Cu, (Δ) high ash conditions, (O) low ash conditions

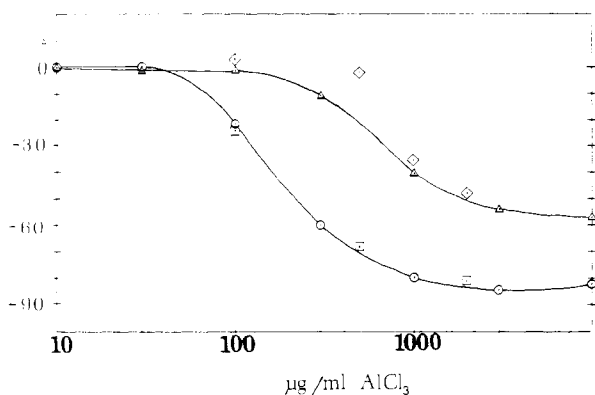


Figure 3. Effect of AlCl_3 on Cu absorbances. (Δ) high ash, 1 $\mu\text{g/mL}$ Cu; (\diamond) high ash, 0.5 $\mu\text{g/mL}$ Cu; (O) low ash, 1 $\mu\text{g/mL}$ Cu; (\square) low ash, 0.5 $\mu\text{g/mL}$ Cu

The high ash curve for MgCl_2 (Figure 4) is the same as the curves for AlCl_3 and has a "normal" shape. The low ash curve, however, is quite different in that it passes through a minimum of $-56\Delta\%$ at about 250 $\mu\text{g/mL}$ and then rises to $-34\Delta\%$ at 10000 $\mu\text{g/mL}$. CaCl_2 shows some indication of a similar effect, the data were however highly scattered.

For several salts, the effect of a matrix was determined on a lower concentration of Cu to determine if the ratio of Cu to interferent or the absolute amount of interferent was the dominant factor. The copper concentrations were varied from 0.1 to 1.0 $\mu\text{g/mL}$. In all cases studied, the same absolute amount of interferent caused the same degree of interference. This is illustrated for 0.5 $\mu\text{g/mL}$ Cu in AlCl_3 and MgCl_2 (Figures 3 and 4). This would indicate that the interference is due to a physical effect rather than a stoichiometrically dependent chemical effect.

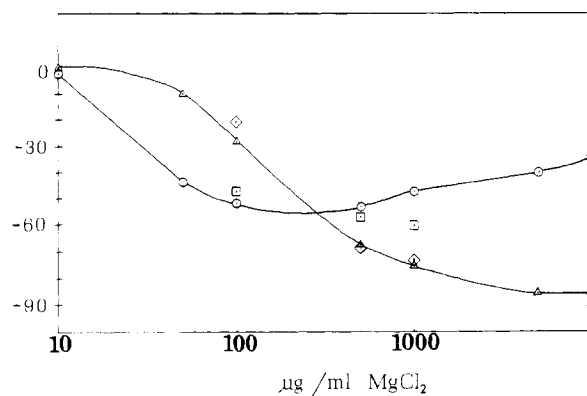


Figure 4. Effect of MgCl_2 on Cu absorbances. (Δ) high ash, 1 $\mu\text{g/mL}$ Cu; (\diamond) high ash, 0.5 $\mu\text{g/mL}$ Cu; (O) low ash, 1 $\mu\text{g/mL}$ Cu; (\square) low ash, 0.5 $\mu\text{g/mL}$ Cu

The results presented thus far are consistently explicable by an interference mechanism dominated by the occlusion of the analyte in matrix crystals. The analyte atoms are trapped in microcrystals or agglomerates of matrix material which is not destroyed in the ash cycle and some fraction of which is large enough to be thrown from the atomizer in the atomize cycle without decomposing to free the analyte.

For the alkali chlorides studied, these microcrystals are most likely chloride or perhaps mixed chloride-oxide species. The similarity of boiling points (and hence vapor pressures and evaporation rates) of LiCl, NaCl, and KCl (1380 $^{\circ}\text{C}$, 1465 $^{\circ}\text{C}$, and 1407 $^{\circ}\text{C}$, respectively) would explain the great similarity of their interference curves. MgCl_2 , CaCl_2 , and AlCl_3 interferences are also consistent with an occlusion mechanism. AlCl_3 upon addition to water evolves HCl and thus the most likely "crystal" to form upon drying is a mixed hydroxide chloride which would become predominantly an oxide matrix during either a high or low ash cycle and thus parallel the behavior of the alkali halides discussed above. The high ash decomposition of magnesium and calcium should also follow this behavior. However, the low ash temperature (350–400 $^{\circ}\text{C}$) is close to the decomposition temperatures of $\text{Mg}(\text{OH})_2$ (350 $^{\circ}\text{C}$) and $\text{Ca}(\text{OH})_2$ (580 $^{\circ}\text{C}$). Thus, several hydrates of the chlorides as well as hydroxides, and hydrated oxychlorides would be favored for the low ash decomposition of these species. Several of these compounds decompose upon heating to release HCl. Thus, as the matrix content of these salts increases, a gelatinous film of matrix would most likely form which would enhance the formation of small crystals of matrix in intimate contact with the graphite cup. This ashing behavior would explain the apparently anomalous behavior of MgCl_2 at low ash and the anomalous and irreproducible behavior of CaCl_2 at low ash. Since CaCl_2 forms mono-, di-, and hexahydrates in addition to $\text{Ca}(\text{OH})_2$ which decomposes just above the low ash temperature, high variability would be expected.

Occlusion is also supported by the nonstoichiometric nature of the salt interferences. Occlusion is a physical process and is not dependent on the stoichiometric ratio of analyte to interferent as are chemical processes.

The effects exhibited for the NaCl interference in the presence of acids are also consistent with occlusion. The HNO_3 could assist in the removal of the salt by forming volatile NaNO_3 and HCl resulting in the observed enhancement. H_2SO_4 and H_3PO_4 are both rather viscous acids and would lower the ionic mobility during the drying process and dry more slowly, resulting in smaller crystals. These smaller crystals have a larger surface area to volume ratio, would have a greater contact area with the carbon cup, would evaporate faster, and would be less likely to occlude the analyte, resulting in less interference. These acids would also

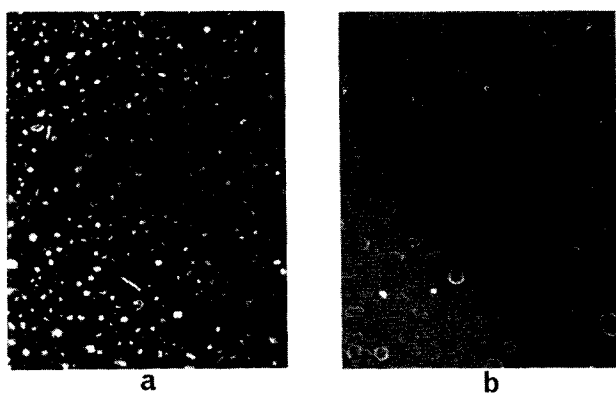


Figure 5. SEM photographs of the sample cup. Low ash conditions, (a) NaCl + 1 M H₂SO₄, (b) NaCl + 1 M H₃PO₄ (See text)

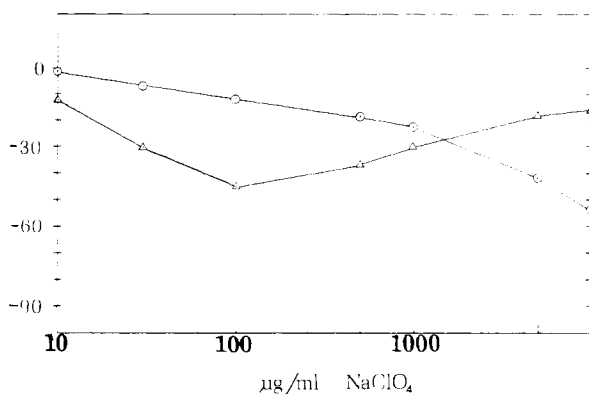


Figure 6. Effect of NaClO₄ on Cu absorbances. 1 µg/mL Cu, (Δ) high ash conditions, (O) low ash conditions.

tend to retain water of hydration in the crystals which upon ashing or atomization would be rapidly vaporized, fracturing the salt crystals and releasing trapped analyte atoms. This effect would be diminished by the more thorough drying of the high ash cycle, as is observed for these solutions.

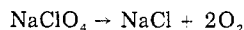
Further evidence of the variation in crystal size formed is seen in Figure 5. These photographs are electron micrographs of the bottom of the graphite cups after low ash cycle. The cups contained 3000 µg/mL NaCl, 1 µg/mL Cu and 1 M H₃PO₄, or H₂SO₄. Both are at ~80× magnification under which each photograph represents ~75% of the surface of the bottom of the cup. Each previously unused cup was fired

4 times to decontaminate, then fired 3 times with the normal dry, ash, atomize settings with the appropriate solution added. A fourth injection of solution was made and the dry and ash cycles were performed. The cup was then removed from the atomizer and the SEM photos were taken. For a comparison of the crystal size obtained for pure 3000 µg/mL NaCl, 1 µg/mL Cu solutions, refer to Figure 9. It is obvious that the acids significantly affect the crystals formed. H₂SO₄ leaves much smaller crystals than pure NaCl, and H₃PO₄ leaves a dust of matrix distributed over the surface of the cup with higher concentrations in the grain boundaries of the graphite.

Such dramatically different crystal sizes led to the investigation of salts which would either evolve gases or produce a gel stage during the dry or ash cycles to determine which process was most likely to produce microcrystalline deposits.

NaClO₄ interfered with the Cu absorbance unlike any other salt tested in this work. Figure 6 is a point-by-point average of five separate sets of NaClO₄ data run at various times throughout the work. The individual curves were always the same general shape and were displaced vertically over a maximum range of 10Δ%. The low ash curve drops off linearly to 1000 µg/mL, then more steeply to a minimum of -66Δ% at 20000 µg/mL. Under high ash conditions the NaClO₄ begins to cause a suppression of the Cu absorbance almost immediately. The interference curve drops off rather steeply to a minimum of -45Δ% at 100 µg/mL, then increases to a maximum of -16Δ% at 10000 µg/mL, then drops off very steeply to -50Δ% at 20000 µg/mL.

Figure 7 shows the cups after low and high ash for 3000 µg/mL NaClO₄. Under low ash conditions, slightly more deposit is left than for the NaCl/acid matrices discussed above. Under high ash conditions the deposits appear finely dispersed and most of the matrix has been destroyed as is evident by the lack of crystals in the X600 magnification (Figure 7c). Only a few extremely small crystals remain near the center of the cup (the round raised mass at the upper left of the photograph). Evidently the matrix is being destroyed by decomposition of the NaClO₄ with fracturing of the crystals and some varying loss of solid material during the high ash. This is consistent with the known decomposition of NaClO₄ at ~650 °C.



Studies of Cu response vs. ash temperature in the presence of NaClO₄ indicated that ash settings between 6 and 7 were necessary to cause the high ash suppression of the Cu signal. This corresponds to a temperature of about 700 °C which is

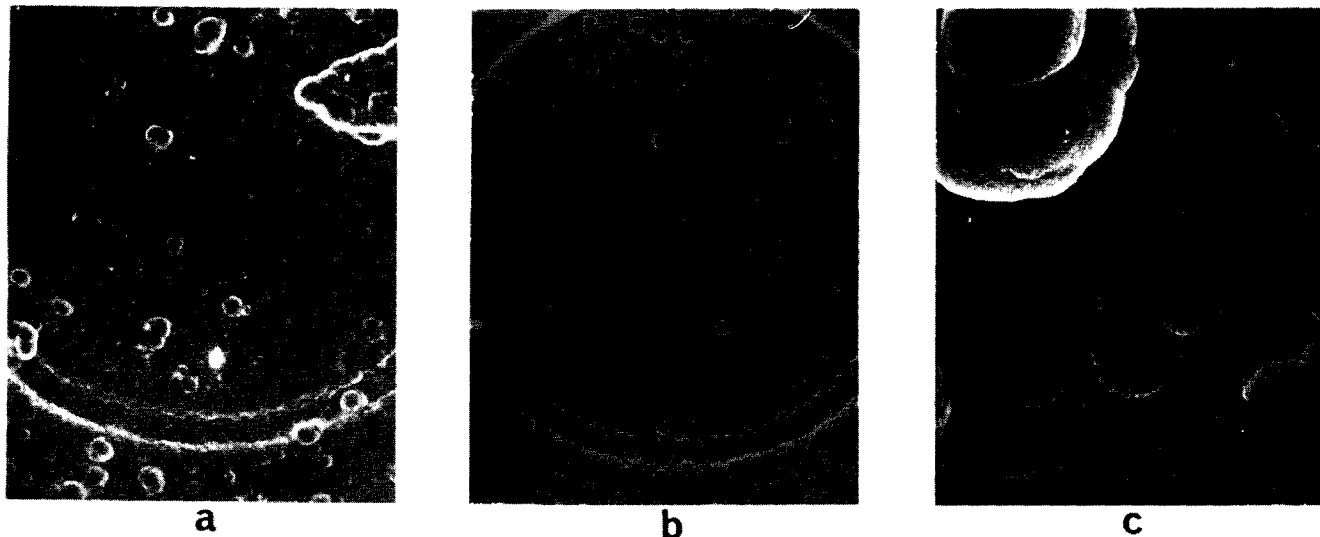


Figure 7. SEM photographs of cups containing NaClO₄. (a) 80X, low ash, (b) 80X high ash, (c) 600X high ash (cup center in upper left corner)

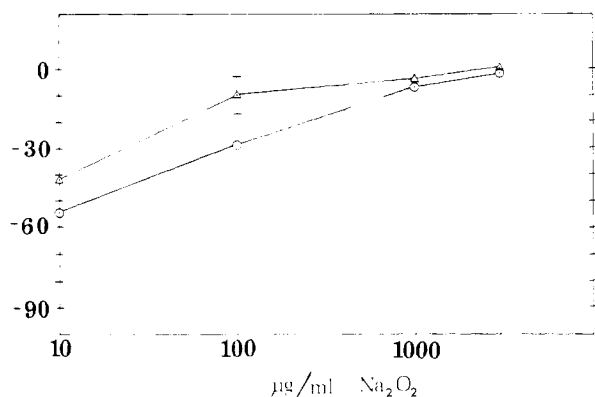


Figure 8. Suppression of the NaCl interference using Na_2O_2 . All solutions contain 1 $\mu\text{g/mL}$ Cu, 3000 $\mu\text{g/mL}$ NaCl, and varying Na_2O_2

Table II. Effect of Na_2O_2 on Interference of Various Salts

Solution	Low Ash		High Ash	
	Peak height	$\Delta\%$	Peak height	$\Delta\%$
Cu only	216.4	—	214.7	—
+ Na_2O_2	189.6	-12.4	200.3	-6.7
Cu + NaCl	90.5	-58.2	149	-30.6
+ Na_2O_2	211.7	-2.2	215.9	+0.6
Cu + NaClO_3	144.6	-24.6	162.5	-9.7
+ Na_2O_2	187.0	-2.6	171.2	-4.9
Cu + NaClO_4	144.2	-39.4	205.6	-13.6
+ Na_2O_2	211.6	-11.1	214.1	-10.0
Cu + AlCl_3	24.0	-90.2	18.8	-91.6
+ $\text{Na}_2\text{O}_2(\text{DI})^a$	189.6	-23.0	190.5	-15.0

^a DI = Double Injection (see text).

very close to the decomposition temperature of NaClO_4 at $\sim 650^\circ\text{C}$. Since the interference effect was different from that of NaCl, the presence of oxygen in the cup during the high ash cycle was implicated as a major factor in the observed interferences. To test this hypothesis, sodium peroxide, Na_2O_2 , was added to the cup as another source of oxygen. The result was the nearly complete elimination of the interferences normally caused by the salts.

Figure 8 illustrates the effect of increasing amounts of Na_2O_2 on the Cu signal in the presence of 3000 $\mu\text{g/mL}$ NaCl. Rather dramatic increases in the signal are observed until at 3000 $\mu\text{g/mL}$ Na_2O_2 , both high and low ash signals are within 2% of the response for the pure Cu solution.

The effect of adding 3000 $\mu\text{g/mL}$ Na_2O_2 to several other salts is shown in Table II. The concentrations of Cu and of salt in all these solutions are 1.0 $\mu\text{g/mL}$ and 3000 $\mu\text{g/mL}$, respectively. These solutions were run at different times and their $\Delta\%$'s are calculated relative to the pure Cu response at that time, not necessarily the one listed in the table. Na_2O_2 suppresses the interference of the salt and improves the signal in all cases. There is very little difference between the response under high ash and low ash conditions.

Figure 9 illustrates the differences in crystal size obtained. The deposits of pure NaCl under low ash conditions are quite large and are diminished only somewhat by the high ash cycle. The addition of sodium peroxide results in a rather uniform covering of small crystals with a few larger deposits. The high ash with Na_2O_2 added results in an extremely fine, uniform powder from which no occlusion occurs.

The oxidizing ability of Na_2O_2 could also play a minor role in its elimination of interferences. In the presence of Na_2O_2 , a heated solution of CuCl_2 dries as the black oxide whereas without Na_2O_2 , it dries as the green chloride. If CuO is formed by the Na_2O_2 during the dry cycle, occlusion would be less

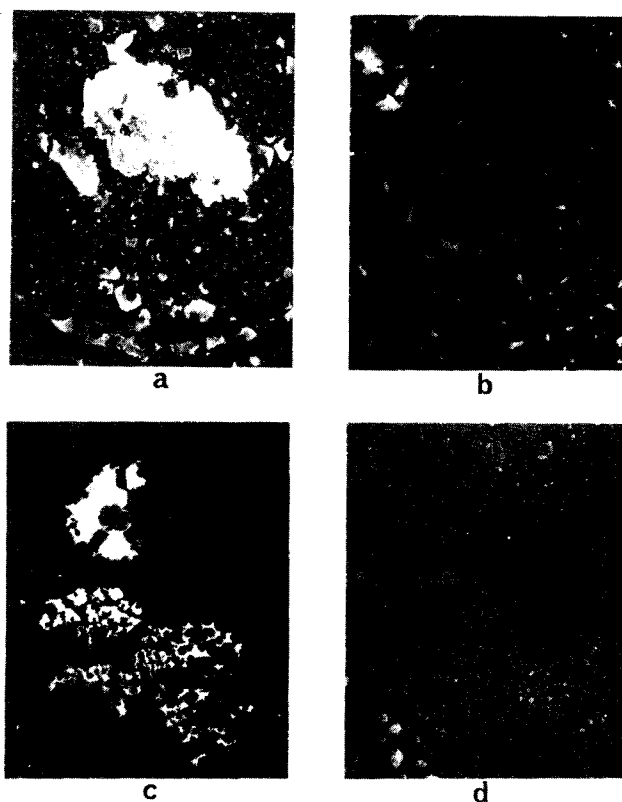


Figure 9. SEM photographs of sample cups. (a) 3000 $\mu\text{g/mL}$ NaCl, low ash; (b) 3000 $\mu\text{g/mL}$ NaCl + 3000 $\mu\text{g/mL}$ Na_2O_2 , low ash; (c) 3000 $\mu\text{g/mL}$ NaCl, high ash; (d) 3000 $\mu\text{g/mL}$ NaCl + 3000 $\mu\text{g/mL}$ Na_2O_2 , high ash

likely because the larger, insoluble CuO molecule would not fit into a forming halide salt crystal as easily or be as available as a Cu^{2+} ion. Na_2O_2 would form oxides of other species in the cup such as the volatile and easily atomized Na_2O which would boil off at high ash temperatures and help to eliminate the matrix. Having all the Cu in the form of CuO would make it more available for carbon reduction as shown by Campbell and Ottaway and others (12, 13).

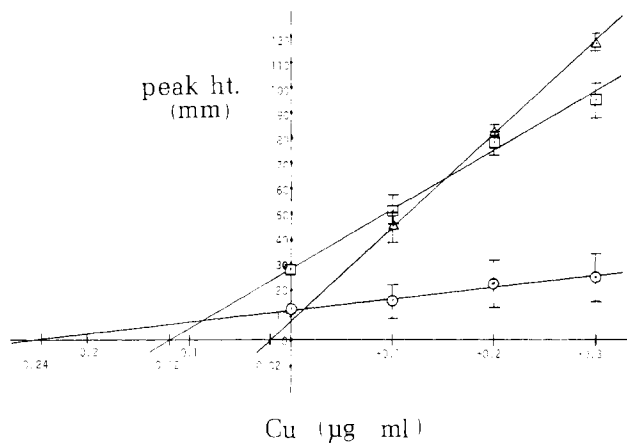
Addition of Sodium Peroxide to Seawater. Seawater is an excellent test of the capacity of Na_2O_2 to remove salt interferences. Synthetic and natural seawater was obtained from the New England Aquarium and samples were spiked with 0.2 $\mu\text{g/mL}$ Cu and with 0.2 $\mu\text{g/mL}$ Cu + 3000 $\mu\text{g/mL}$ Na_2O_2 . The addition of both the Cu and the Na_2O_2 resulted in a 14% dilution of the seawater.

The results shown in Table III indicate once again that the Cu signal is improved in all cases by the addition of Na_2O_2 . Recovery of the Cu signal is not quite as complete with the seawater as it was with the salt solutions but the total concentration of salt (36900 $\mu\text{g/mL}$ for synthetic seawater) is also much greater. Considering this concentration of salts, the recovery is remarkable.

Na_2O_2 was also added to the spiked seawater by a double injection technique (signified by DI in Table III) whereby the seawater sample is injected into the cup in the normal manner, then a 5- μL volume of 3000 $\mu\text{g/mL}$ Na_2O_2 solution is also injected, and the dry-ash-atomize sequence is initiated. This results in the same amount of material in the cup as with the premixed method and simplifies solution preparation. However, it requires very careful adjustment of the dry voltage and time settings so that the solution dries completely without boiling out of the cup. With both the synthetic and natural seawater, this double injection technique resulted in a greater improvement in the signal than the premixed method, perhaps because the Na_2O_2 has had less time to decompose.

Table III. Effect of Na_2O_2 on Response of Cu in Seawater

Solution composition	pH	Low ash			High ash		
		Peak ht	$\Delta\%$	RSD	Peak ht	$\Delta\%$	RSD
Pure 0.2 $\mu\text{g/mL}$ Cu	3	81	—	1.9	79	—	2.5
0.2 $\mu\text{g/mL}$ Cu + 3000 $\mu\text{g/mL}$ Na_2O_2	12.5	66.5	-17	0.5	64.5	-18	1.1
Synthetic seawater	6.5	0	—	—	0	—	—
Syn. + 0.2 $\mu\text{g/mL}$ Cu	4.5	48.3	-40	8.6	34.0	-45	10.8
Syn. + Cu + 3000 $\mu\text{g/mL}$ Na_2O_2	10	59	-27	6.7	76	-4	15.6
Syn. + Cu + $\text{Na}_2\text{O}_2(\text{DI})^a$	—	72.4	-10	4.0	73.3	-7	11.3
Natural seawater	6.5	0	—	—	0	—	—
Nat. + 0.2 $\mu\text{g/mL}$ Cu	4.5	9.6	-89	3.5	11.8	-85	6.0
Nat. + Cu + 3000 $\mu\text{g/mL}$ Na_2O_2	10	59.3	-31	10.8	61.8	-21	7.6
Nat. + Cu + $\text{Na}_2\text{O}_2(\text{DI})^a$	—	63.3	-26	18.2	70.3	-10	1.9
Nat. + Cu + 3000 $\mu\text{g/mL}$ $\text{NaOH}(\text{DI})^a$	—	50.3	-41	1.8	56.0	-28	16.8
Nat. + Cu + 30% $\text{H}_2\text{O}_2(\text{DI})^a$	—	27.3	-68	7.1	30.3	-61	4.1

^a DI = Double Injection (see text).Figure 10. Standard addition analysis of seawater for Cu. (Δ) blank; (O) high ash, no Na_2O_2 ; (\square) high ash, 3000 $\mu\text{g/mL}$ Na_2O_2

When Na_2O_2 is added to water, some of the Na_2O_2 reacts to form NaOH and O_2 , causing the solutions to become very basic and effervesce. There is also a slow evolution of oxygen from the solutions upon standing. Because of this, the effect of NaOH alone was determined with natural seawater. The addition of 3000 $\mu\text{g/mL}$ by double injection resulted in an improvement of the Cu signal but not to the extent of the Na_2O_2 improvement (Table III). The spiked seawater was also run with 30% H_2O_2 by double injection and this resulted in an improvement of 20 $\Delta\%$ —the smallest improvement of all.

One of the most common methods for compensating for matrix effects is the method of standard additions. To determine what effect the presence of Na_2O_2 would have on standard additions plots, natural seawater spiked with 0.1 $\mu\text{g/mL}$ Cu was analyzed with and without the addition of 3000 $\mu\text{g/mL}$ Na_2O_2 . The standard addition plots, Figure 10, show rather dramatically the advantages to be gained by the addition of Na_2O_2 . The graph for seawater with Na_2O_2 gives a value for the Cu concentration of 0.12 $\mu\text{g/mL}$ which, when corrected for the standards blank, becomes 0.10 $\mu\text{g/mL}$ —exactly the amount added. Without Na_2O_2 , however, the value obtained is 0.24 $\mu\text{g/mL}$ —twice the actual value. This graph also has larger standard deviations for the individual points and is less sensitive because of the very small slope of the line. The addition of Na_2O_2 to the seawater clearly enhances the precision and accuracy of the analysis.

It is evident that the physical size and chemical composition of a sample/matrix deposit can dramatically affect the signal achieved. Occlusion of the analyte in the matrix is the predominant mechanism of interference. Occlusion is reduced by compounds forming smaller crystals by forming viscous gels upon drying (NaOH , H_3PO_4 , Na_2O_2 , HNO_3), by forming unstable crystals which fracture via gas evolution (MgCl_2 , Na_2O_2 , NaClO_4), by forming volatile matrix compounds (Na_2O_2 , HNO_3 , NaClO_4), or by a combination of these. Adding one compound to a matrix to cause one of the above effects is in some instances advantageous. For example, L'vov (17) has added LiNO_3 to some NaCl matrices and found a decrease in interference.

However, such additions must be made with caution as evidenced by the results of large excesses of NaClO_4 in this study. It appears that addition of a substance which provides a uniform dispersion of extremely small crystals is the most desirable matrix interference suppresser. The only obvious alternative is to use an atomizer which has an extremely long pathlength so that crystals containing occluded analyte are totally decomposed before exiting the atomizer. Studies employing long pathlength atomizers and extending the present study to include more volatile elements and other potential interference suppressers are currently under way.

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