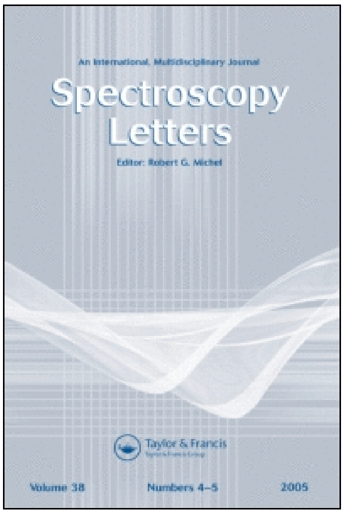

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Matrix Effects in Laser Ablation-Direct Current Argon Plasma Emission spectrometry-Some Preliminary Observations

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MATRIX EFFECTS IN LASER ABLATION - DIRECT CURRENT ARGON PLASMA EMISSION SPECTROMETRY - SOME PRELIMINARY OBSERVATIONS

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ABSTRACT

The emission intensity of copper and manganese in a solid sample determined by laser ablation - direct current argon plasma emission spectrometry is dependent on the type of compound and concentration of matrix (sodium halide). At a 100x level of matrix to analyte, a depression of 50-70% occurs. The higher the density of the analyte compound, the lower the emission intensity signal. The higher the density of the matrix, the greater the depression.

INTRODUCTION

Recent communications describe a laser ablation - direct current argon plasma emission spectrometric system for the direct determination of metals in solid samples [1-4]. Detections limit were in the μg g^{-1} range, linear dynamic range over several orders of magnitude, precision under 10% and acceptable accuracy obtained by standard additions. However, it was noted that different copper compounds with the same concentration of copper gave different slopes of calibration curves and the use of calibration curves could only be used if the matrix of the unknown samples and standards were similar[1]. Obviously, the matrix composition of a sample was effecting the signal from the system. Wennrich et al[5] noted a matrix interference when studying laser atomic absorption spectrometry in a graphite furnace.

This report describes preliminary observations on the effect of different matrices and different compounds on the copper and manganese signal from laser ablation - direct current argon plasma emission spectrometry.

EXPERIMENTAL

The laser ablation - direct current argon plasma emission spectrometric system has been fully described elsewhere[1-4] and consists of a Nd: YAG laser (Laser Photonics Inc., Orlando, FL) operated at a wavelength of 1.06 μm, an energy of 100 mJ per pulse, a pulse rate of 20 Hz, power delivered of 2W and a beam diameter of 6.35 mm, and a Spectrametrics Spectraspan V, direct current argon plasma emission single channel echelle monochromator with a 3-electrode plasma jet (Beckman Instruments, Somerset, NJ). A laboratory made ablation cell held the solid sample and connected the laser to the plasma[3]. Sample preparation involved weighed portions of cellulose (binder), analyte compound, and matrix thoroughly mixed in a ball mill and compressed at 10000 psi for insertion into the ablation cell[1]. The mass of the pellet was constant for all experiments and each result was the mean of three trials with a precision of under 10%. All chemicals were "Baker Analyzed" reagents (J. T. Baker Chemical Co., Phillipsburg, NJ). The copper emission line a 324.7 nm and manganese emission line at 279.5 nm was monitored.

RESULTS AND DISCUSSION

(a) Effect of Various Sodium Halide Concentrations on Copper Emission Signal

The effect of increasing concentration of various sodium halides on a constant concentration of 1000 $\mu g\ g^{-1}$ of copper (as copper (II) chloride) is shown in FIG. 1. There is no significant deviation in the emission signal when the sodium halide concentration is less than the copper concentration. However, as the concentration of sodium halide increases over the concentration of copper, a depression in the copper emission signal occurs, and at 100x concentration of sodium halide to copper, a reduction of 50-70% occurred (depending on sodium halide). A larger concentration of sodium halide would not

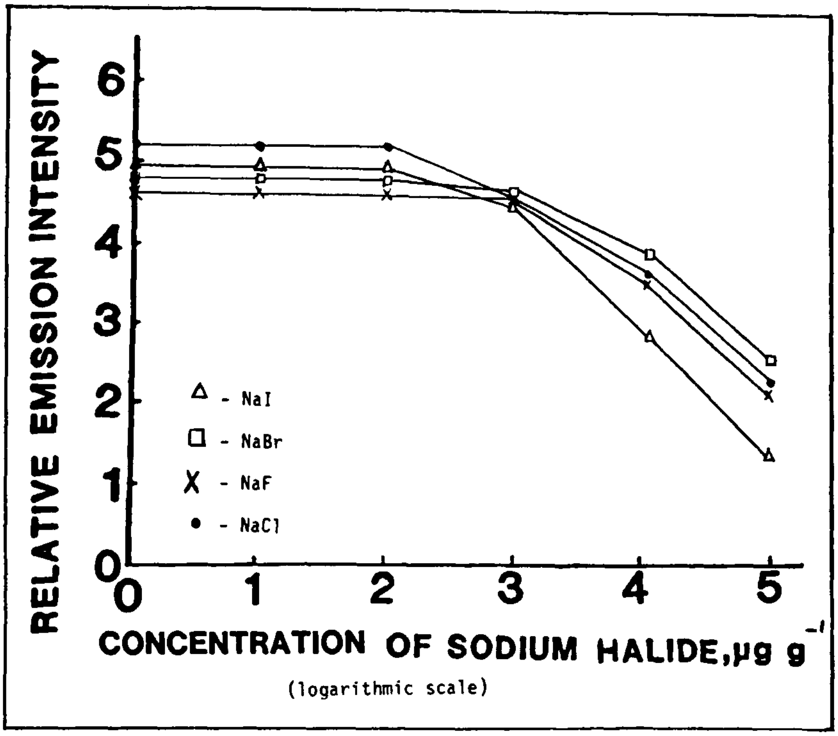

FIG. 1. The effect of increasing concentration of sodium halides on copper emission intensity at 324.7 nm.

produce a pellet due to lack of cellulose which prevented binding, but it is reasonable to assume that the greater the ratio of sodium halide to copper, the greater the magnitude of the depression. An examination of the results of FIG. 1 show that the magnitude of the depression increases NaI > NaF > NaCl > NaBr and approximately correlates with the trend in density of the sodium halides but not the boiling points (shown in Table 1). It is probable that the pellet with the highest density (NaI) causes the lowest emission intensity and the pellet with the lowest

Table 1

Boiling Point and Density of Compounds Used for Matrix Effect Studies[6]

Compound	Boiling Point, K	Density, g cm^{-3}
NaF	1695	2.56
NaCl	1413	2.17
NaBr	1390	3.20
NaI	1304	3.67
$Mn(C_2H_3O_2)_2$	--	1.74
$MnCl_2$	1190	2.99
$MnCO_3$	--	3.12
$MnSO_4$	850	3.25
MnS	--	3.99
MnO_2	--	5.03
Mn	1962	7.20
$CuCl_2$	993d	3.39

density (NaF) causes the highest emission intensity. In all cases, where the density of the pellet is increased, a depression will occur - the magnitude depending on ratio of analyte to the matrix. These results support previous work[1] which postulated that high density particles would be more likely to settle out by gravity, in transversing the distance from the ablation chamber to the plasma. It appears that the density of the matrix has a similar effect to different compounds of an analyte.

(b) Effect of Different Manganese Compound on Emission Intensity

Previous results showed that different compounds containing the same concentration of copper gave different copper emission

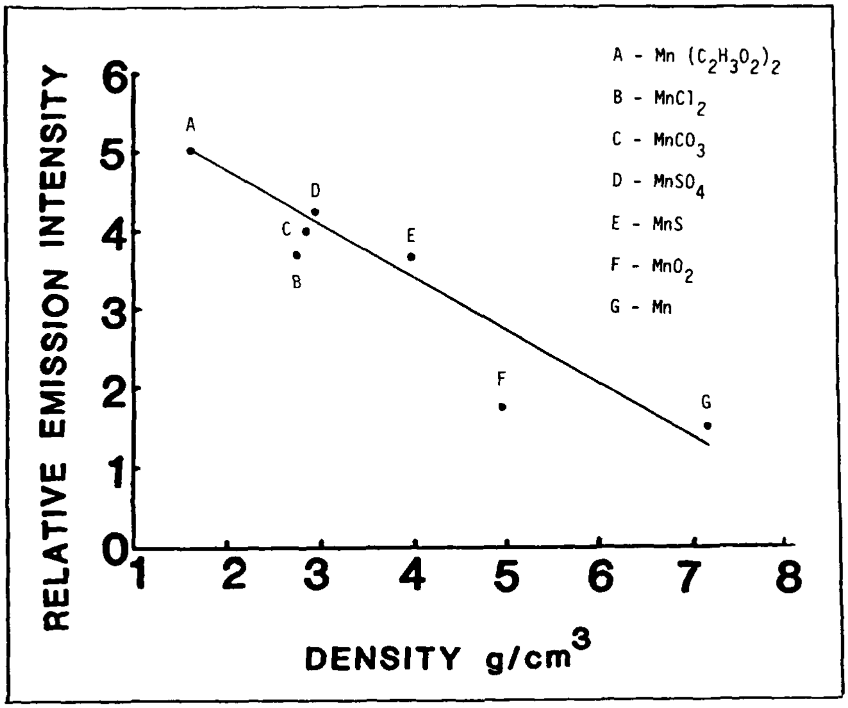

FIG. 2. Variation in emission intensity with density of various manganese compounds.

signals[1]. A similar experiment for a constant concentration of 1240 µg g^{-1} of manganese with different manganese compounds was performed and the results plotted versus the density of manganese compound shown in FIG. 2. The regression equation is on the form of Y = BX + A where Y is the dependent variable of relative emission intensity and X the density of different manganese compounds. The equation from the data was Y = -0.64X - 0.46 with a correlation coefficient of 1.06. These results support previous work on copper based on the densities of the analyte compounds.

Table 2

Effect of Different Sodium Halides on Emission Intensity from Different Manganese Compounds[A]

Compound	Matrix	Relative Emission Intensity
Mn	Cellulose	1.30
Mn	Cellulose + NaCl	1.18
Mn	Cellulose + NaI	1.21
MnO_2	Cellulose	4.02
MnO_2	Cellulose + NaCl	3.69
MnO_2	Cellulose + NaBr	3.73
MnO_2	Cellulose + NaI	3.73
$MnSO_4$	Cellulose	1.52
$MnSO_4$	Cellulose + NaCl	1.32
$MnSO_4$	Cellulose + NaI	1.33

[A] A manganese concentration of 1240 $\mu g\ g^{-1}$ and sodium halide concentration of 1000 $\mu g\ g^{-1}$.

(c) Effect of Different Sodium Halides on Emission Intensity from Different Manganese Compounds

The effect of different sodium halides on the emission intensity of manganese metal, manganese dioxide, and manganese sulfate is shown in Table 2. In all cases, the introduction of sodium halide concentration reduced the relative emission intensity of the particular manganese compound by 8-13%, depending on the halide and manganese compound. While different sodium halides had slightly different effects, the relative magnitudes were not considered sufficient to support the hypothesis that the density of the matrix effects the emission intensity.

CONCLUSION

The emission intensity of copper and manganese in a solid sample by laser ablation - direct current argon plasma emission spectrometry will depend on the copper and manganese compound being determined. A depression in emission signal will occur depending on the concentration of matrix (sodium halide), the magnitude increasing with increasing ratio of matrix to analyte. Results for copper and manganese compounds, and sodium halides suggest that the density of the solid sample is the major cause of this interference. It is possible that a laser which has a higher energy than 100 mJ per pulse may minimize or reduce these effects. Research is continuing on matrix effects with the current system and a new system using a higher energy per pulse laser is being planned.

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