

Application of a Membrane Desolvator to the Analysis of Organic Solvents in Inductively Coupled Plasma Atomic Emission Spectrometry

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A micro porous PTFE membrane desolvator (MMD) was built and evaluated for the on-line removal of organic solvents to facilitate the determination of trace metal contaminants in the solvents by ICP-AES. Three organic solvents, isopropyl alcohol (IPA), methanol, and dimethyl sulfoxide (DMSO) were studied. The MMD reduced organic solvent concentration in the sample aerosol stream by 82% to 89%, as indicated by monitoring C(I) emission. Net signal intensity of Fe, Al, and Cu was increasing with higher organic solvent concentration, with the rate of increase being solvent dependent. The signal intensities for Mg and Pb followed the trend with the C(I) signal. Changing the sweep gas flow rate affected the optimum signal intensity. Wine samples were analyzed by the method of standard addition. The concentrations of B, Al, and Mg were determined with a relative precision of less than 2.3%.

Introduction

The use of a membrane desolvator is becoming a widespread sample injection technique in inductively coupled plasma atomic emission spectrometry (ICP-AES) as well as inductively coupled plasma mass spectrometry (ICP-MS).¹⁻³ It gives better precision due to damping absorption, shows less acid interference effect, and reduces solvent loading. The effect of organic solvent load on the analytical parameters, for example, axial emission profile, radial spatial profiles of solvent and analyte species and noise power spectra were studied by D. G. Weir and M. W. Blades.^{4,7}

Various kinds of membrane desolvators for solvent removal have been developed and showed excellent performance. A silicon membrane with a concentric nebulizer (Meinhard) showed the solvent removal efficiency in the range of 80% to 100% for Freon, chloroform, methanol, and ethanol.⁸⁻¹¹ A hygroscopic nafion membrane that is nonporous and allows small polar molecules to pass through was also used to reduce solvent loading.¹²⁻¹⁴ Recently a tubular micro porous PTFE membrane has been used to remove the nebulized vapor of various organic solvents, including hexane, methanol, THF, acetone, and dichloromethane.¹⁵⁻¹⁸ The membrane desolvator is usually coupled to a ultrasonic nebulizer (USN) or a microconcentric nebulizer (MCN) with a heated spray chamber. In general, the use of the membrane desolvator increases signal intensity and decreases the background. Another means of reducing organic solvent loading is by cooling the spray chamber using a cryogenic desolvator. Cryogenic desolvation was reported to remove chlorides in the aqueous solvent more extensively than the membrane desolvation.¹⁹

A method for the determination of rare earth elements in wine by ICP-MS without a membrane desolvator was reported.²⁰ In that work the wine sample was evaporated to remove ethanol and reconstituted the ratio of water to ethanol for matrix matching and introduced by flow injection

method with the typical flow rate of 30 $\mu\text{L}/\text{min}$.

In this work a micro-porous PTFE membrane desolvator was built and studied for the analytical performance by introducing organic solvents in MCN-ICP-AES. The optimization of the operating conditions and the efficiency change of solvent removal were studied. For an application, commercially available wines were analyzed to determine trace elements using MCN-ICP-AES with the membrane desolvator. At this time the samples were prepared by the standard addition and directly introduced into the system.

Experimental Section

The instrument employed in this study was a Jovin-Yvon (model: JY 138) ICP-AES. This system was equipped with a 40.68 MHz generator with a standard torch including a sheath gas flow and a 1m focal length nitrogen-purged monochromator. It was operated at 1.1 kW forward power with a coolant flow of 12 L/min. A microconcentric nebulizer (model MCN-100, Cetac, USA) was used at the sample uptake rate of 250 $\mu\text{L}/\text{min}$. A Scott type double pass spray chamber was cooled to 3 °C to reduce solvent overloading. There was no carbon deposition or disturbing the plasma observed at this condition. The optimized operating condition was listed in Table 1.

A membrane desolvator was built with a PTFE tube of 3.0 mm i.d. (Gore Tech., USA) and a glass tube of 8 mm i.d. that was heated by means of a heating tape wound around it. The length of the membrane tube was 0.8 m. The flow rate of argon for sweep gas could be adjusted by two ball flow meters for inlet and outlet. No additional nitrogen gas was used for aerosol gas flow to increase the plasma excitation capability. The measured elements and each wavelength were listed in Table 2.

All the chemicals used in this work were analytical grade (Sigma-Aldrich, USA) or ultrapure grade (Dongwoo Chemical Co., Korea). Viton® peristaltic tubing (Labcraft, Jobin

Table 1. Instrumental operating conditions in ICP-AES

ICP	Operating conditions
Model	JY 138 (Jovin Yvon)
Generator	Frequency : 40.68 MHz Forward power : 1.1 kW
Torch	Demountable type with sheath gas flow Coolant gas flow : 12 L min ⁻¹ Auxiliary gas flow : 0.1 L min ⁻¹ Aerosol gas flow : 0.9 L min ⁻¹ Sheath gas flow : 0.2 L min ⁻¹ Observation height : 15 mm
Nebulizer	Nebulizer : microconcentric nebulizer (MCN-100, Cetac) Spray chamber : Scott type water-cooled double pass, -3 °C maintained Sample uptake rate : 0.3 mL min ⁻¹
Membrane desolvator	PTFE membrane tubing .8m in length 3 mm i.d. heated to 160 °C
Optics	Czerny-Turner mount 1.0 m focal length 2400 grooves/mm second order grating nitrogen purge type

Table 2. The measured elements and wavelengths

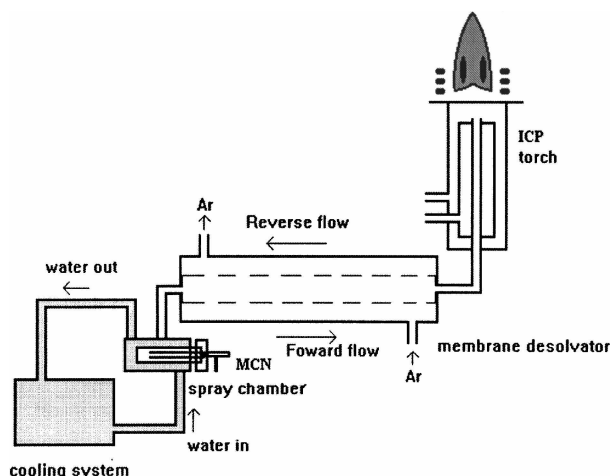
Elements	Wavelength (nm)
Al (I)	309.278
B (I)	249.773
C (I)	247.856
CN	388.340
Cu (I)	324.754
Fe (II)	259.940
Hg (II)	194.227
Mg (II)	279.553
Mg (I)	285.213
Ni (I)	341.476
Pb (II)	220.353
Si (I)	251.611
V (II)	310.230

Yvon, France) was used to introduce all the organics except methanol for which Ismaprene® tubing was used. Bottles of wine (Jinro Co., Korea) were purchased from the market. Standard addition for calibration using NIST CRMs (3101a, 3126a, and 3131a) was employed. The mixture of water and ethanol, the same ratio as the constitution of wine sample, was prepared for dilution and blank solution. All the samples and standard solutions were acidified with 0.1% HNO₃.

Results and Discussion

Membrane desolvator (MMD) for solvent removal.

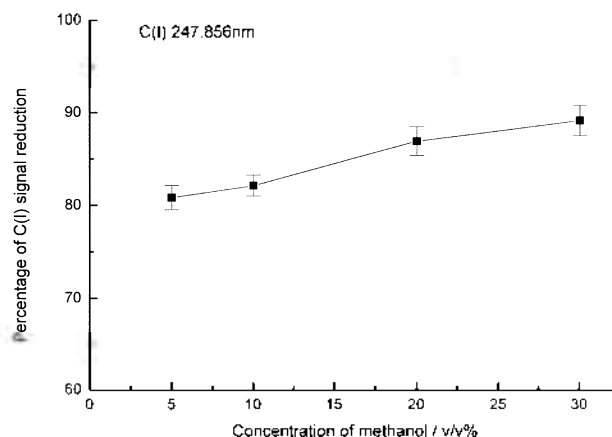
The standard introduction system was modified by adding a membrane desolvator in-line between the water-cooled spray chamber (3 °C) and the ICP torch, as shown in Figure

**Figure 1.** Modified sample introduction system in ICP-AES

1. Solvent vapors passed through the membrane and were carried away by a flow of Ar sweep gas.

To test the efficiency of solvent removal, the relative intensity of C(I) (247.856 nm) emission was determined with and without the laboratory-built MMD (Figure 1). The sample flow rate was 250 μ L/min, the minimum necessary to minimize pulsation from the peristaltic pump. Although the solvent flow rate was higher than values reported previously for ICP-MS,² the use of an ICP-AES instrument in this work allowed such high flow rates to be used. Without the MMD the ICP could not be sustained at IPA concentration above 30%, whereas 100% IPA samples could be analyzed with the MMD. For the purpose of comparing solvent removal efficiency, the organic solvent concentration was restricted to between 0% and 30%. In this experiment the outlet gas flow was not restricted.

Figure 2 plots the reduction of C(I) emission intensity vs. the concentration of methanol when using a sweep gas flow rate of 1.1 L/min. Carbon emission was reduced by 82% for a 5% methanol solution increasing to 89% reduction for 30% methanol. These values are comparable to or worse than the solvent removal efficiencies reported by other

**Figure 2.** The change of the reduction percentage of C(I) signal with an increase of the methanol concentration.

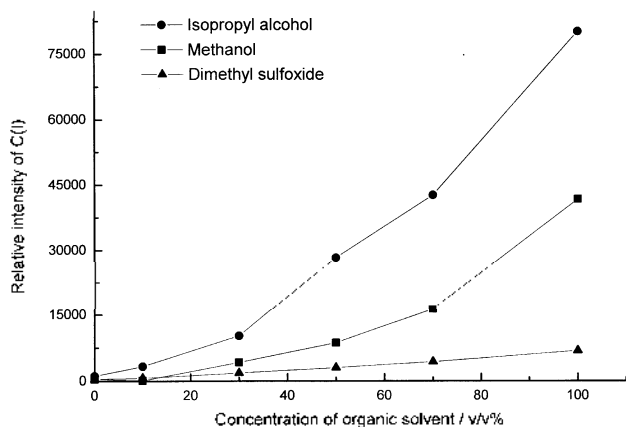


Figure 3. The change of C(I) intensities of methanol, isopropyl alcohol, and dimethylsulfoxide when the concentration of the solvents increased.

workers,^{8,9} but may be related to saturation effects caused by the higher sample flow rates used in our experiment.

Effect of solvent. Figure 3 plots the intensity of C(I) as the concentration of each of the three organic solvents is increased up to 100%. The C(I) intensity is lowest for DMSO and increases linearly. For IPA and methanol the C(I) intensity is higher and increases non-linearly. The

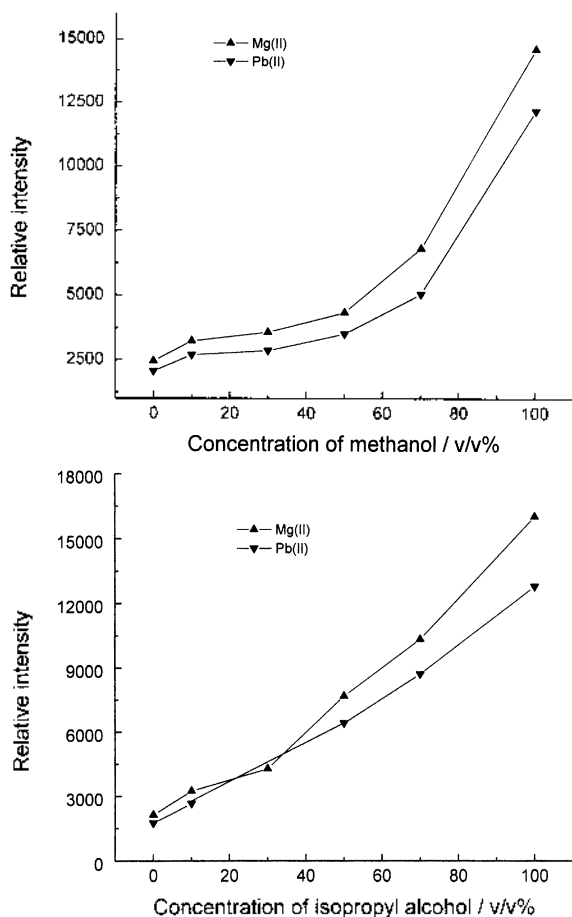


Figure 4. The change of Mg and Pb intensities of methanol, isopropyl alcohol when the concentration of the solvents increased.

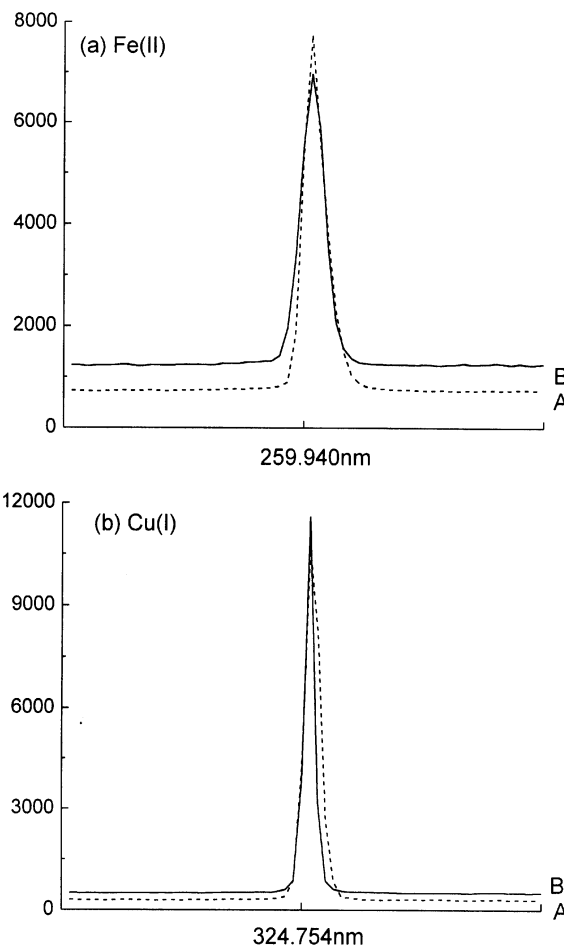


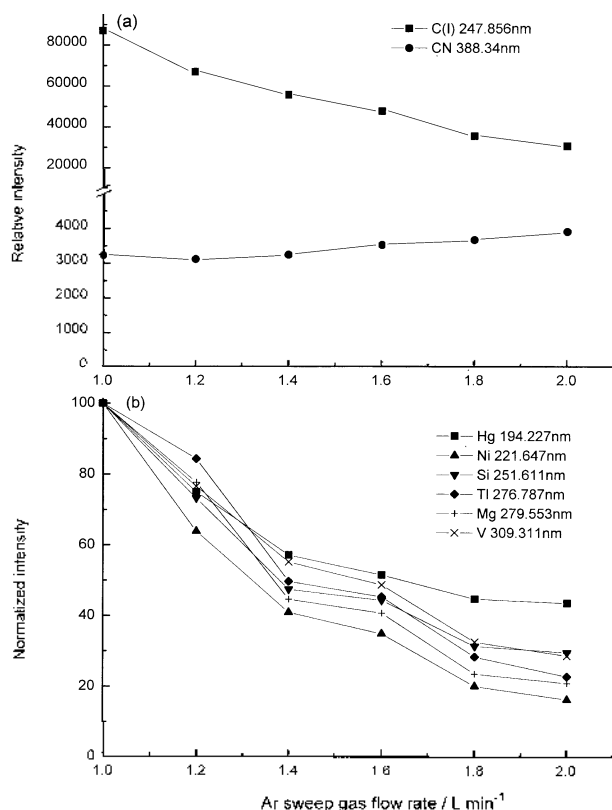
Figure 5. A spectrum of 1 $\mu\text{g}/\text{mL}$ Fe (a) and Cu (b) in 30% ethanol with (A) and without (B) the Membrane desolvator.

higher intensity is likely related to the higher vapor pressure for these two solvents (b.p. 64.7 $^{\circ}\text{C}$ for methanol and b.p. 82.5 $^{\circ}\text{C}$ for IPA) compared to DMSO (b.p. 189 $^{\circ}\text{C}$). With IPA and methanol more solvent leaves the cooled spray chamber and enter the MMD. The non-linear effects may indicate partial saturation of the membrane with solvent vapors. Analyte signal from Pb and Mg increases as the solvent concentration increases, as shown in Figure 4. It means that the more organic droplets were introduced into the plasma as the solvent concentration increased.

Figure 5 shows the reduction in continuous emission background for 1 $\mu\text{g}/\text{mL}$ Fe and Cu in 30% ethanol. Using the MMD reduced the background level and enhanced the analytical emission of Fe, Al, and Cu, but not Pb. Table 3 shows the signal to background (S/B) ratios for the elements measured with and without using the MMD. The S/B ratios of Cu and Fe with the membrane improved almost two times compared to those without the membrane, but the improvement was relatively small for Pb. The relative standard deviation (RSD) with the membrane was obtained in the range of 1-3%, whereas it was higher than 5.0% without the membrane. In the latter case even though the sample uptake rate was reduced to below 30 $\mu\text{L}/\text{min}$, the plasma could not be sustained for more than 10 min due to the carbon deposition.

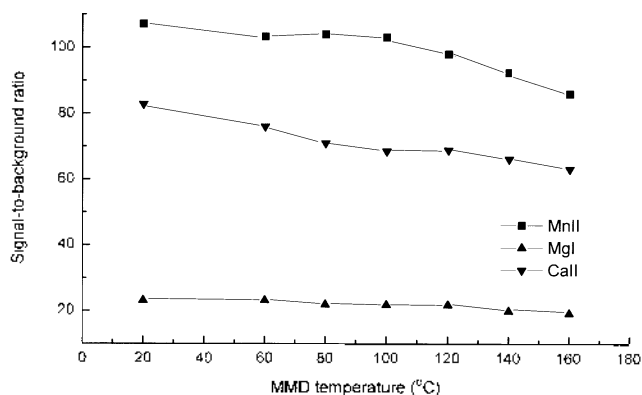
Table 3. Signal to background ratios of 1 ppm Cu, Al, Pb, and Fe in 30% ethanol

Membrane Desolvator	Signal to background ratios			
	Cu	Al	Pb	Fe
With	10.25	3.28	4.21	50.6
Without	5.49	2.19	3.68	25.3

**Figure 6.** The intensity change of trace elements in isopropyl alcohol with an increase of sweep gas flow rates in MCN-ICP-AES: (a) for C and CN. (b) for trace metals.

The memory effect for sample introduction system was studied by the measurement of the time required for the signal reduction of 1 $\mu\text{g/mL}$ Pb to the baseline. The reduction times of 30 s and 75 s for 1% and 0.1% of the original intensity, respectively, were obtained and those were close to that obtained by other workers.^{14,15}

Optimization of MMD. Once the plasma was stabilized, little effect of the sweep gas flow on the net intensities was reported in ICP-AES. In this experiment, the change of net intensities of C(I), CN, Ni, Si, Tl, Mg, V, and Hg in IPA with an increase of the sweep gas flow rate is illustrated in Figure 6. All other solvents, such as, ethylene glycol (EG), and dimethylsulfoxide (DMSO), showed the similar behaviors. As shown in the figure, increasing the sweep gas flow suppressed the net intensities of the elements measured whilst the intensity of CN increased slightly. A possible reason for the reduction is that the unbalanced Ar flow between the sweep gas and the aerosol gas had an influence on the change of the emission zone and the residence time of ana-

**Figure 7.** The effect of desolvation temperature on the analyte signal in 100% isopropyl alcohol.

lytes in the plasma. However, it was discussed by other workers that the reductions of analyte intensities seen at higher sweep gas flow rates were not due to changes of the aerosol gas flow caused by the sweep gas flow.²¹ It should be noticed that the reduction trend obtained in this experiment differed compared to the results obtained by them. By a possible mechanism analytes could be lost in the membrane desolvator. In this case analytes were adsorbed on the membrane or removed with the organic solvent. There is no evidence at this time to suggest which might be dominant.

The effect of desolvation temperature on the signals of Mn, Mg, Ca in IPA was evaluated as the temperature was varied to 160 °C. The results are illustrated in Figure 7. As shown from the figure, the net intensities of all the lines decreased by 12-20% with increasing temperature.

Direct analysis of organic samples. Calibration curves for the determination of B, Al, Mg, and Fe were made at the various concentrations of ethanol. The R-coefficients were obtained to be 0.9994 for deionized water, 0.9998 for 30% methanol, 0.9995 for 50%, 0.9990 for 70%. The slopes of the calibration curves increased with an increase of the concentration of ethanol because more organic droplets were introduced into the plasma.

For an application, wine samples were analyzed in this experiment. The direct introduction of wine into the ICP without a membrane desolvator for a long time encountered problems of carbon deposition and plasma instability. The analysis of wine using an ICP-MS was reported by Augagneur, *et al.*²⁰ In that paper, a typical flow rate of 30 $\mu\text{L/min}$ was used and total 100 μL of sample was consumed by flow injection method. And, for the sample pretreatment, the wine was evaporated to remove ethanol and reconstituted the ratio of water to ethanol for matrix matching. In this work the samples were prepared by the standard addition and directly introduced into the system. Table 4 is showing the analytical results of wine using the MCN-ICP-AES with the membrane desolvator. Since sample 1 and sample 2 were from different bottles and manufactured with grapes produced at different dates and places, no coincidence was existed in the results. In both bottles the concentrations of B, Al, and Mg were high enough to be determined in ICP-AES. Iron was

Table 4. Analytical results of Korean wine samples by ICP-AES (unit: $\mu\text{g/mL}$)

Sample	B	Al	Mg	Fe
#1	1.30 (1.7) ^a	0.747 (1.3)	13.8 (2.3)	— ^b
#2	1.44 (1.6)	0.342 (1.3)	13.4 (2.0)	0.860 (1.5)

^arelative standard deviation (%) of 5 times measurements. ^bnot detected.

detected in sample 1, but not in sample 2. Rare earth elements were not observed in this work due to the lack of sensitivity. As shown in the table, all the elements were determined with a relative precision less than 2.3%.

Conclusion

The lab-built MMD was effective enough to analyze volatile organic samples directly in ICP-AES with the MCN. Solvent removal efficiencies of a PTFE membrane were obtained to be dependent upon chemical and physical property of organic solvents. As the flow rate of an Ar sweep gas increased, the signal intensities of the analytes decreased and the reduction trends were similar to each other. Both precision and rinse-out times were generally comparable to the reported values.

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