Study of Sample Solvent/Carrier Combination for Flow Injection Analysis-Atomic Absorption Spectrometry

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Abstract

The use of thirteen solvents, both as sample solvents and liquid carriers in flow injection analysis with atomic absorption, was studied. Five primary alcohols, three secondary alcohols, four ketones and water were used as sample solvents and liquid carriers in the system. The determination of copper using this system was demonstrated. The relative FIA-AA signals of 169 combinations of sample solvent-liquid carrier pairs are reported. A ten-fold increase in the signal relative to the aqueous system was achieved using 3-pentanone or butanone as sample solvent with methanol carrier. An 8.9-fold increase in the signal of aqueous copper solutions was achieved when n-butanol was used as liquid carrier. Nine calibration curves were constructed using nine different solvent-carrier pairs. It was found that the optimum flow conditions of one system may not be optimum for others. A relative precision between 0.8% and 4.7% was achieved. Further optimization of the experimental conditions may give better sensitivity.

Introduction

Atomic absorption spectrophotometry is still the technique of choice in analyzing for metals in many analytical laboratories.[1-5] The determination of the levels of many metals in physiological fluids is of high clinical and diagnostic significance.[2-5] The metal level is, sometimes, too low for direct analysis and special techniques are required to achieve the analyses.[3,4] Some modifications have been introduced to the atomic absorption technique to make it capable of detecting these low limits. These modifications include the use of electrothermal atomization,[1,3,6] Zeeman background correction,[5] sample decomposition[7] and sample preparation, which includes chelation of the metal ions followed by extraction into an organic solvent.[8] Flow injection analysis is the technique of choice if fast analysis, high reproducibility and low reagent and/or sample consumption are required.

The feasibility of flow injection analysis with atomic absorption means of detection has been demonstrated and well established.[7,9,11-14] The use of a flow injection analysis-atomic absorption (FIA-AA) system with nonaqueous solvents and carriers was also demonstrated[12]. Four organic solvents and water were used as sample solvents and as liquid carriers. A significant enhancement of the signal was achieved, relative to the aqueous

system, when a nonaqueous or partially nonaqueous system was used. Copper was used as an example. Optimization of the sample volume and the length of the mixing coil was made.[12] A follow-up study using other solvents and other metals was needed.

In this study, thirteen solvents were studied as sample solvents and liquid carriers, and demonstrated to be useful in the determination of copper by flow injection analysis with atomic absorption detection. A total of 169 combinations of sample solvent-liquid carrier pairs are reported. The effect of flow rate on the FIA-AA signal of 30 sample solvent-liquid carrier pairs was studied. A ten-fold enhancement of the signal compared to the aqueous system was achieved. Best results can be achieved if the optimum flow conditions for each sample solvent-liquid carrier pair are determined and followed.

Experimental

Reagents

Copper stock standard solutions of 1000 ppm from E. Merck Daimstadt were used to prepare all copper standards. Ethanol, n-butanol, n-pentanol and 3-pentanone were from E. Merck Daimstadt; 3-pentanol and methylisobutyl ketone (MIBK) were from Fluka-AG-Chem Fabrik; n-propanol and butanone were from Cambrian Chemicals Co.; acetone and 2-propanol were from Koch Light Limited; 2-butanol was from BHD Chemicals, Ltd.; and methanol was from Hopkin and Williams. Aqueous solutions were prepared using distilled, deionized water.

Apparatus

A Perkin-Elmer 372 Atomic Absorption Spectrophotometer with strip chart recorder was used for all the studies. Teflon tubing of 1 mm i.d. from Beckman Altex was used in the flow system. A 50 μl loop injector from Valco Instrument Co, Houston, Texas, was used to introduce the sample into the flowing stream. Glass syringes of 5, 3 and 1 ml volumes were used to introduce the samples into the injector loop. The mixing coil was 30 cm long and connected the injector loop with the port of the atomic absorption nebulizer. No pump was used; instead, the negative pressure of the nebulizer was utilized to draw the carrier liquids from the reservoirs to the injector and to the burner of the AA spectrophotometer. The atomic absorption operating conditions are given in Table I.

Table I: Experimental Conditions for the FIA-AA system used.

Wavelength; 324.7 nm	Lamp current; 25 mA
Slit; 0.7 mm	Flame; air–acetylene
Burner; premix nebulizer burner	Observation height; 6 mm above the burner

Gas flow; acetylene 1 l/min
           air   8 l/min for water, methanol and ethanol carriers; 10 l/min for the rest of the carriers
Recorder out put 10 mV

Procedure

Copper standards in the different solvents were prepared by dilution of the stock solution in the appropriate solvent. With the exception of water, methanol, ethanol and acetone solvents, a few drops of ethanol were added to help dissolve the water droplets from the stock solution in the other organic solvents. Copper standards of 2, 4, 6, 8 and 10 ppm copper in each of the solvents were used to construct of the calibration curves. Five parts per million copper standard solutions were used to compare the signals and to study the effect of the flow rates and of the different combinations of samples solvents and liquid carriers. The FIA signals with the different carriers were obtained by immersing the pumping tube in the carrier reservoir and injecting the sample solution into the carrier using the injector. The liquid carrier carries the sample plug into the burner of the atomic absorption spectrophotometer. The flow rate was adjusted using the nebulizer port. The flow rates used were 5.0 ml/min. for the methanol carrier, 6.5 ml/min. for 3-pentanone carrier and 5.5 ml/min. for the rest of the carriers. A sample volume of 50 μl was used for all measurements. All other operating conditions of the FIA-AA system were kept constant for all the studies except the air flow rate, which was 8 l/min. when water, methanol and ethanol carriers were used and 10 l/min. when the rest of the organic solvents were used as carriers.

Results and Discussion

Figure 1 depicts the calibration curves for the determination of copper in aqueous solution by using distilled water, methanol, 2-propanol, n-pentanol and n-butanol, respectively, as carriers. Comparing curves A and E shows an increase of 8.9-fold in the FIA-AA signal of a copper aqueous solution by choosing the appropriate carrier. The enhancement of the signal is due to the organic solvent effect[12] and to limited dispersion for those solvents with restricted miscibility with water.

Figure 2 depicts the calibration curves for the determination of copper in different solvents, water, n-propanol, methanol, acetone and 3-pentanone, using methanol carrier. The calibration curve of copper in aqueous solution using water carrier is included as reference for comparison. A 10.7-fold enhancement of signal was achieved when 3-pentanone solvent and methanol carrier were used. Again, the enhancement of the signal is believed to be due to organic solvent effect and different dispersion rates.

Table II shows the relative FIA-AA signals for 169 sample solvent/carrier combinations for 13 solvents used. The signal of water solvent/water carrier was taken as unity, and the rest were calculated relative to it. Precision ranges from 0.8% for the n-propanol solvent/2-propanol carrier system to 4.7% for the n-butanol solvent/n-butanol carrier system. It is apparent from the table that, in general, the ketones are better solvents, while methanol, ethanol, 3-pentanone and MIBK are better carriers. It can also be seen that 3-pentanone sample solvent and methanol carrier is the best combination for enhanced signal. And n-butanol is the best carrier for aqueous copper solutions, while 3-pentanol is the best sample solvent if water is to be used as a carrier. When an aqueous solution of copper was used,

the order of the carriers in enhancing the FIA-AA signal was: n-butanol > n-pentanol > 3-pentanol > 2-butanol > MIBK > 3-pentanone > n-propanol > 2-propanol = butanone > ethanol > methanol > acetone > water.
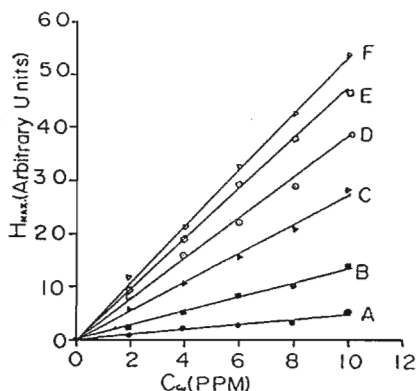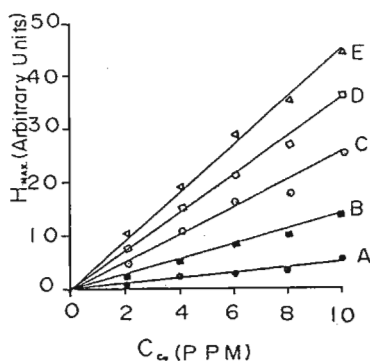

Fig. 1   Calibration curves of copper standard solutions in water using different carriers: (A) water, (B) methanol, (C) 2-propanol, (D) n-pentanol, (E) n-butanol.

Fig. 2   Calibration curves of copper standard solutions in water (A and B), n-propanol (C), methanol (D), acetone (E), and 3-pentanone (F), using water carrier in (A) and methanol carrier in the rest.

Table II: Relative FIA-AA signals of the different solvent/carrier combinations. The signal of water solvent in water carrier was taken as unity.

Carrier / Solvent	H_2O	CH_3OH	C_2H_5OH	$n\text{-}C_3H_7OH$	$2\text{-}C_3H_7OH$	$n\text{-}C_4H_9OH$	$2\text{-}C_4H_9OH$	$n\text{-}C_5H_{11}OH$	$3\text{-}C_5H_{11}OH$	acetone	butanone	3-pentanone	MIBK
H_2O	1	6.0	6.1	6.3	7.3	8.5	5.9	6.7	9.4	7.5	6.5	7.5	6.0
CH_3OH	2.7	7.7	6.5	5.4	6.9	4.7	5.7	4.1	4.9	9.6	10.0	10.7	8.1
C_2H_5OH	4.3	7.5	6.7	5.5	6.7	4.8	5.2	3.8	4.3	6.9	7.7	8.0	7.3
$n\text{-}C_3H_7OH$	5.3	8.6	5.6	5.2	4.8	4.0	4.0	2.9	3.3	5.7	4.6	5.3	4.3
$2\text{-}C_3H_7OH$	5.0	5.4	5.3	4.2	4.3	3.8	3.9	2.7	3.6	5.1	5.7	6.4	5.3
$n\text{-}C_4H_9OH$	8.9	3.7	3.3	3.1	2.7	2.6	2.7	2.0	1.9	4.4	4.8	4.4	3.3
$2\text{-}C_4H_9OH$	6.3	4.9	4.3	4.0	3.7	7.8	2.7	2.3	2.3	5.4	8.3	5.0	3.7
$n\text{-}C_5H_{11}OH$	7.0	3.1	3.3	2.7	2.7	2.3	2.3	2.1	1.7	3.4	3.3	3.7	2.0
$3\text{-}C_5H_{11}OH$	6.7	3.1	2.8	2.2	2.3	1.7	1.4	1.3	1.7	3.0	3.3	3.7	2.1
acetone	2.2	7.8	6.8	3.7	5.6	3.0	3.6	2.3	3.0	7.1	4.9	4.4	6.0
butanone	5.0	7.3	5.6	5.7	5.0	3.7	5.0	3.4	4.0	6.7	6.4	5.0	3.3
3-pentanone	5.7	9.7	8.3	8.7	8.3	8.3	8.4	5.9	7.7	8.7	9.2	7.8	4.2
MIBK	5.8	9.6	9.4	7.9	8.7	7.5	7.7	6.0	6.0	9.5	8.9	7.2	6.2

Figure 3 shows the effect of flow rate for 5 ppm copper in six solvent/carrier combinations. Curve 3-A shows the flow rate of copper solution in 3-pentanone using methanol carrier. It was found that with all sample solvents, the signal comes to a minimum at a flow rate around 4 ml/min, using this carrier. The quantitative variations of the signal with flow rate is not the same for all sample solvents. Acetone, for example, gave a higher signal than butanone when the flow rate was between 3.5 and 4.0 ml/min, but at higher or lower flow rates, the opposite was the case. It was observed with this carrier that ethanol solution gave a higher signal than methanol solution at flow rates below 2.8 ml/min, while the opposite is observed at higher flow rates. It was shown that the FIA-AA signal varies with the composition of the solvent if a mixture is used as solvent[12]. This variation of the signal with the different solvents and flow rates may be attributed to different mixing rates and formation of a mixture-like sample solvent.

Curves 3-B–3F, respectively, show the effect of flow rate on the signal of 5 ppm copper solutions for the following solvent/carrier combinations: 3-pentanone in ethanol, ethanol in n-propanol, acetone in butanone, acetone in 3-pentanone and ethanol in MIBK. It was found that, generally, all the sample solvents behaved qualitatively similarly in affecting the variation of the signal with the flow rate of a given carrier, although the absolute magnitude of the signals varied (Table II).

It is shown in this figure that the relative signals for many solvent systems are highly dependent on the flow rate. This means that the optimum flow rate of a solvent in a carrier is not necessarily the same for another solvent, even in the same carrier. The optimum flow rate must be determined after the solvent/carrier combination pair is chosen. The information in Table II was obtained under the conditions described in the Experimental section. Better results could be achieved using the optimum flow rate of each sample solvent in every carrier.

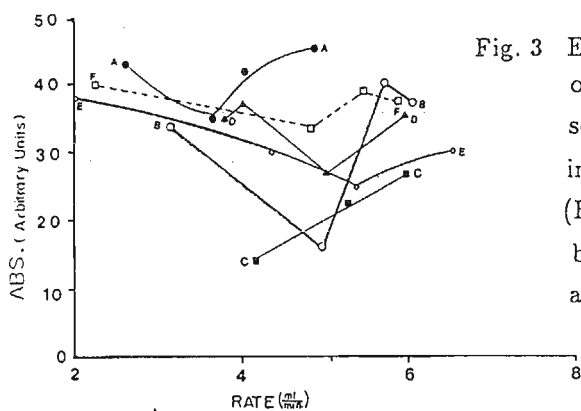Sample volume and the length of the mixing coil were optimized in a previous study.[12]

Fig. 3 Effect of flow rate on the FIA-AA signal of 5 ppm Cu solutions in the following solvent/carrier combinations: 3-pentanone in methanol (A), 3-pentanone in ethanol (B), ethanol in n-propanol (C), acetone in butanone (D), acetone in 3-pentanone (E) and ethanol in MIBK (F).

Figure 4 shows the effect of the number of carbon atoms of the solvent on the relative signals of 5 ppm Cu solutions in primary alcohols (4-I) and secondary alcohols (4-II) using primary alcohol carriers. It is shown that for a given carrier the signal decreases as the number of carbon atoms of the solvent increases. It is also shown that the order of carriers in enhancing the signal with a given solvent is: methanol $\geq$ ethanol $>$ n-propanol $>$ n-butanol $>$ n-pentanol.

Figure 5 shows the effect of the number of carbon atoms of the solvent on the relative FIA-AA signal of copper in primary alcohols (5-I) and secondary alcohols (5-II) when secondary alcohols were used as carriers. Again, for a given carrier, an increase in the number of carbon atoms of a solvent results in a decrease in the FIA-AA signal. Also, an increase of carbon atoms in the carrier's molecules causes a decrease in the FIA-AA signal. Figure 6 shows the effect of the number of carbon atoms in the FIA-AA signal of copper in alcohol solvents when ketones were used as carriers. The trend of decreasing the signal as the number of carbon atoms increases is almost preserved. The higher ketones, 3-pentanone and MIBK (Cand D), are the best carriers when both primary and secondary alcohols are used as solvents.

Figure 7 shows the effect of the number of carbon atoms of ketone solvents on the relative signal of copper when primary alcohols (7-I) and secondary alcohols (7-II) carriers were used. The 3-pentanone solvent is the optimum for all these carriers, except 2-propanol, where butanone is the best solvent. Figure 8 shows that for ketone solvents, with ketone carriers, the lower ketones, acetone and butanone are the better solvents, while the higher ketones, 3-pentanone and MIBK (Cand D) are the better carriers.
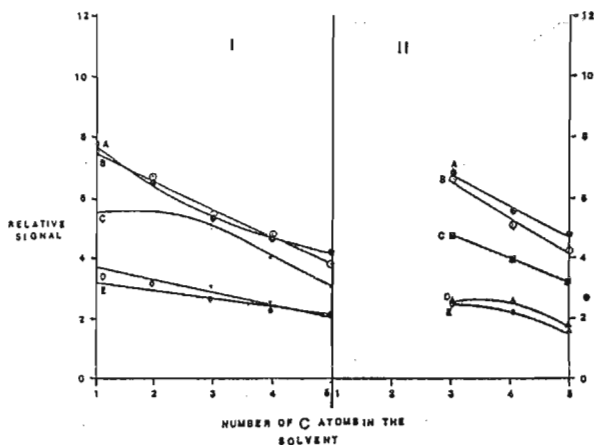

Fig. 4   Effect of number of carbon atoms of primary (I) and secondary (II) alcohol solvents on the relative copper signal when methanol (A), ethanol (B), n-propanol (C), n-butanol (D) and n-pentanol (E) carriers are used.
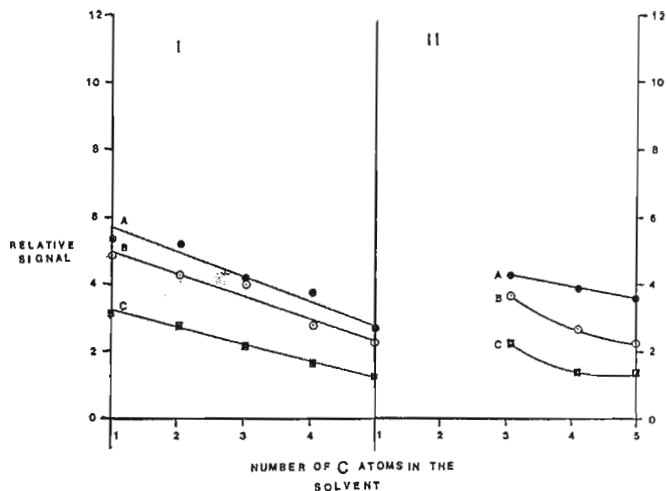
Fig. 5　Effect of number of carbon atoms of primary (I) and secondary (II) alcohol solvents on the relative copper signal when 2-propanol (A), 2-butanol (B) and 3-pentanol (C) carriers are used.
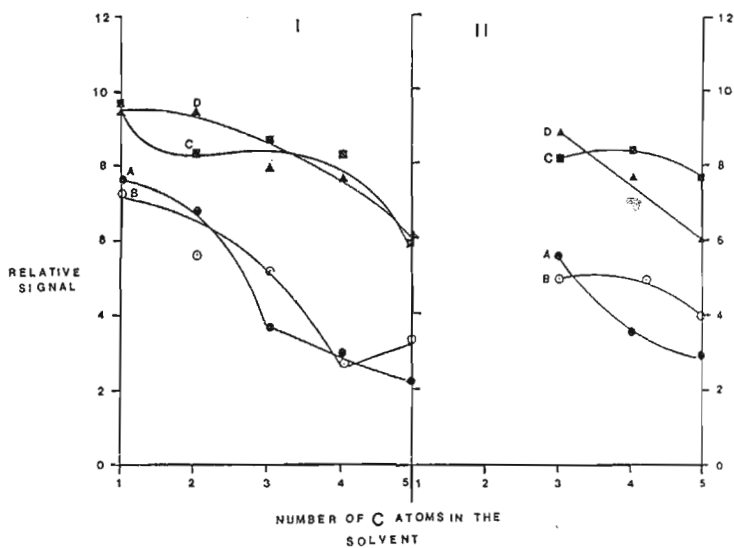

Fig. 6　Effect of number of carbon atoms of primary (I) and secondary (II) alcohol solvents on the relative copper signal when acetone (A), butanone (B), 3-pentanone (C) and MIBK (D) carriers are used.
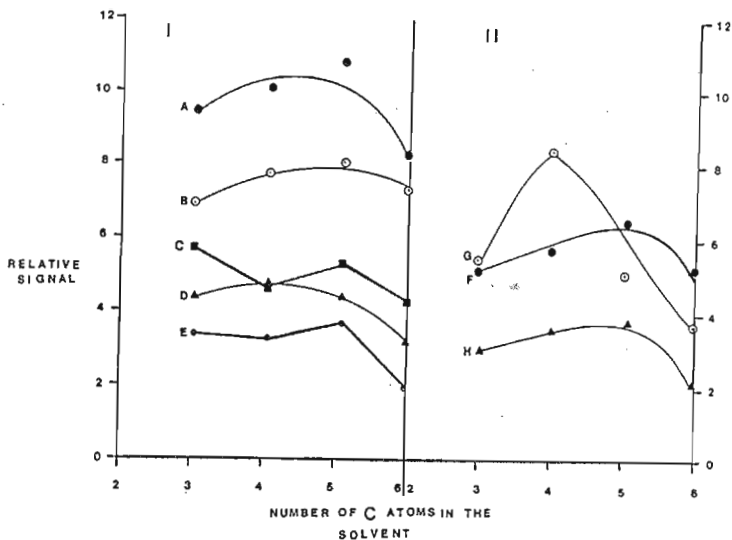
Fig. 7 Effect of number of carbon atoms of ketone solvents on the relative copper signal when alcohol carriers are used: methanol (A), ethanol (B), n-propanol (C), n-butanol (D), n-pentanol (E), 2-propanol (F), 2-butanol (G) and 3-pentanol (H).
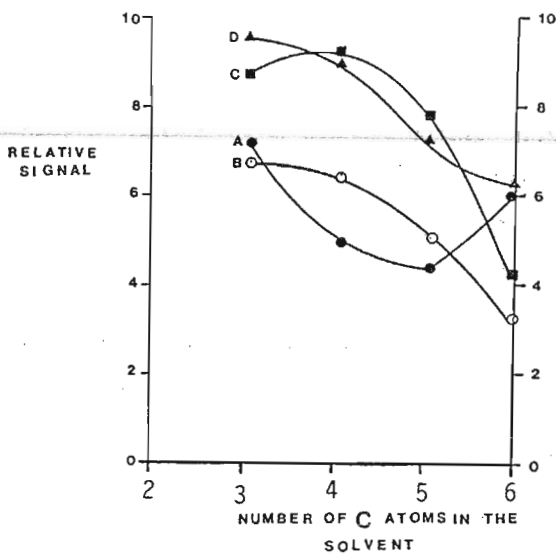

Fig. 8 Effect of number of carbon atoms of ketone solvents on the relative copper signal when acetone (A), butanone (B), 3-pentanone (C) and MIBK (D) carriers are used.

The peak width at the baseline ranges between 10 sec. for water and the low molecular weight carriers to 5 sec. for the higher molecular weight ketones. This enables the analyst to perform more than 300 measurements per hour.

This method is precise and achieves more than a 10-fold increase in sensitivity, which permits lower detection limits and more dilution of samples (smaller samples). Aqueous samples may be extracted with the sample solvent to be injected (provided it is water immiscible) using an appropriate chelating agent. For water miscible solvents, the sample would have to either be diluted by the solvent or a salting out technique could be used.[15] The low viscosity of the organic solvents decreases the viscosity of dispersed samples to a degree to enable analyses of certain samples without further sample preparation. This method does not require any material or instrument that does not already exist in the average analytical laboratory.

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