Organic Solvent Effect for Atomic Absorption Sensitivity

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Abstract

The organic solvent give greatest sensitivity enhancement were used in solvent extraction studies. When extracting (100ml) of aqueous solution with (50ml) of organic solvent. It is possible to detect silver at 5x 10^{-3} ppm, Galium at 4x10^{-3} ppm, Germanium at 8x10^{-3} ppm and copper at 2x10^{-3} ppm based up on the original aqueous phase concentration by using flame atomic absorption technique. Silver, galium, germanium and Copper standard curves were prepared by extraction (100ml) of aqueous solution with (20ml) of organic solvent. Enhancement of atomic absorption sensitivity have been observed in most cases.

الخلاصة

تم استخدام العديد من المذيبات العضوية بدلا من المحلول المائي بطريقة الاستخلاص بالمذيب تؤدي الى زيادة حساسية القياس وبالتالي تؤدي الى تقدير تراكيز صغيرة جدا بالمحلول .

في هذا البحث تم تحويل المذاب الموجود في (100ml) من المحلول المائي الى (50ml) من المذيب العضوي وبهذه الطريقة تم تعيين تراكيز واطئة جدا للعناصر قيد الدراسة. حيث تم تحسس تركيز تصل الى 0.002 ppm Cu, 0.004 ppm Ga, 0.008 ppm Ge, 0.005ppm Ag باستخدام تقنية الامتصاص الذري اللهبي لأغراض القياس. أما منحني المعايرة للمحاليل القياسية للعناصر قيد الدراسة فقد تم تحويل النموذج من (100ml) محلول مائي الى (20ml) محلول عضوي وقياس تركيز العناصر بأستخدام نفس التقنية. وقد لوحظ زيادة الحساسية في اغلب الحالات بعد تحويل النموذج الى الطور العضوي مقارنة مع قياسها وهي بالمحلول المائي.

Introduction

The use of organic reagents in the flame offers the advantages of, a: formation of metal derivatives which are more volatile and more readily dissociable. b: decomposition of the reagents to give products which improve the characteristic properties and increase the temperature of the flame (1-6). Reduction of the analyte to pure metal or metal carbide however, effects the sensitivity of the method, because the volatility of such species decreases in the order oxide > metal > carbide. Organic solvents have been used in studying the effect of solvent extraction on atomic absorption sensitivity(7-9). Enhancement effects have been observed in most cases . All workers have studied selected extraction systems for silver, gallium, germanium and copper, Enhancement was observed in most cases. Hieftje (11-13) Copeland and de Olivares describe extraction systems for many metal ions, the mechanism of this enhancement have revealed that the organic modifies the combustion processes in several ways. The purpose of this study was to survey a number of complexing agent – solvent systems in order to determine the best systems to use for Ag,Ga,Ge and Cu to determine the extent to which the sensitivity can be enhanced for the metal ions using combination solvent extraction and atomic flame absorption spectrometry.

Experimental

1- Reagents

Using standard aqueous solutions of 500ppm silver, gallium, germnium and copper were prepared from the pure (98-99%) metals from different chemical company (BDH and Fluka). Acid dissolution (0.2N HCl) of the accurately weight metal followed by dilution to volume deionized water was used in all cases. Standard germanium and gallium solution were prepared by dissolving an accurately weighted quantity of reagent grade copper dichloride in 0.2 N tartaric acid. The solution low than 500 ppm were prepared daily by dilution of the stoke solution. Organic solutions of copper were prepared from reagent bis (1-phenyl-1,3-butadien) copper and organic solutions of silver were prepared by silver nitrate. Organic gallium and germanium. Solution were prepared from carefully dried reagent gallium and germanium per chlorate.

2- Apparatus

Using ash atomic from all absorbance measurements by atomic absorption-flame emission spectrophotometer model 2380 (perkin-elmer) .Air-acetylene and nitrogen-hydrogen flames were used .

All PH measurement were made using a sergeant model MS PH- meter. Deionized water from Almansur company. Weightings were made on a meter model 4200M digital analytical balance.

3- Procedure

Standard solutions of all metal ions aqueous, and organic solvents, were prepared as described in the reagents section the complexing agents were normally dissolved in the organic solvent for extraction. The aqueous solutions of cupferon and sodium diethyl dithio carbamate(DEDC) were prepared for extractions as they are quite in soluble inorganic solvents (Table 1) show the complexing agents and their concentrations used for the extraction of each metal ion.

Table (1) The complexing Agent used

No.	Metal	Complexing agents	Conc.
1.	Silver Ag	1-Nitrose-2-naphthol cupferon	0.08 M 0.1 M
2.	Gallium Ga	8- hydroxy quinoline diethyl dithio carbamate salt	0.1 M 0.06 M
3.	Germanium Ge	Diethyl dithio carbamate salt 8- hydroxy quinoline	0.1 M 0.12 M
4.	Copper Cu	Cupferon 8- hydroxy quinoline	0.02 M 0.02 M

To determine the optimum conditions for extraction of silver, gallium, germanium and copper. A10 ml of the appropriate standard solution and (10 ml) separating funnel.

(20 ml) of the given solvent containing the chelating agent were

added table (2). The mixture was mixed by mechanically shaker for 15 min. After separating the two layers ,the organic phase was analyzed for metal content and determined the percent extraction.

The PH of the aqueous phase was measured with PH-meter and recorded as the PH of the extraction. After that percent extraction vs PH plot was made. In order to optimize the instrumental parameters ,a standard solution was aspirated and the fuel flow rate varied ,while holding the other three variables constant –until an optimum value was obtained. A blank was aspirated and the instrumental zeroed perior to reading the absorbance at each setting .In like manner, the other three variables, oxidant gas flow rate, burner height, and lamp current, were optimized. Enhancement the sensitivity for each organometallic solvent pair was then obtained by dividing the absorbance reading of a standard aqueous solution into the absorbance reading of a standard organic solution of equal metal concentration.

Germanium and Gallium (Ge,Ga) were extracted by the above procedure and then back-extracted. The organic phase was placed in a 100 ml separating funnel and 10 ml of the aqueous stripping solution added. The solutions were mechanically shaken for 15 min. and then allowed to stand 10 min.

The organic layer was discarded. The aqueous layer was analyzed for metal content and the percent back extraction and percent overall extraction were determined.

After measuring the PH of the initial extraction ,the aqueous solution was analyzed for metal content and the percent initial extraction determined – PH vs. percent plot was made. A standard curve was prepared for each metal studied by plotting absorbance vs. conc., Data abstained by extracting a series of solution containing the metal of various concentrations. The concentration ranges for each metal are given in Table (2).

Table (2) : concentration ranges of metals for preparation of calibration curves

No.	element	Aqueous phase Conc.	Organic solvents
1-	Silver (Ag)	0.005 - 0.003 ppm	Dibutyl ether
2-	Germanium (Ge)	0.008 - 0.004 ppm	Isopropyl acetate
3-	Gallium (Ga)	0.0008 - 0.001 ppm	Isopropyl acetate
4-	Copper (Cu)	0.002 - 0.004 ppm	2- heptanone

The extractions were performed at the optimum PH of extraction and the absorbance readings made at the optimum instrumental settings. A concentration of 100 ml to 2 ml was employed. In all cases, both the aqueous and the organic solvent (Dibutyl ether, Isopropyl acetate and 2- heptanone) were presaturated with each other prior to extraction of the metal ion. This is mandatory in order to eliminate mutual solubility effects.

Results and Discussion

In this study show, the variables considered are fuel flow rate, burner height, oxidant gas flow rate and the hollow cathode. In general, the optimum oxidant flow rate does not very a great deal from solvent to solvent. The type of flame required for atomization of the element determine the optimum fuel flow rate. The optimum range, in most cases is narrow when burner elevation is decreased, there is a sharp increase in sensitivity until an optimum value is found. Then there is generally an optimum range of (3-6 mm) before the sensitivity begins to decrease and the noise level to increase.

The optimum lamp current for each metal does not vary settings for each metal (Ga,Ge,Ag,Cu) studies.

Table (3) show the optimum instrumental conditions

No.	Metal	solvents	Acetylene flow rate L/ min	Air flow rate L/ min	Burner hight mm	Lamp. current mA
1-	Ga	Toluene	1.12	7.82	2.8	6.0
		n- butyl ether	3.11	6.92	1.5	6.0
		Aceton	1.8	6.59	1.7	6.0
2-	Ge	Ethyl isobutyl ketone	1.35	7.2	1.6	4.0
		n-butyl acetate	1.76	6.45	1.8	4.0
		2- octanone	1.22	6.86	1.2	4.0
3-	Ag	Water	6.85	8.22	4.9	12.0
		Butyraldehyde	2.24	7.95	2.2	12.0
4-	Cu	Toluene	8.20	8.33	4.3	14.0
		Butyraldehyde	1.95	8.64	2.6	14.0

Large enhancements may be achieved because higher absorbance readings are generally obtained during use the organic solvents than in aqueous solution and because of the possibility of concentrating the dissolved metal ion species in the organic phase.

A suitable organic solvent was used for atomic absorption determinations should be combustible, and the combustion products should not absorb radiation from the hollow cathode lamp. Carbon tetra chloride (CCl_4) and $CHCl_3$ are commonly used for many metal extractions but are not suitable from atomic absorption because of their unfavorable combustion characteristics – water solvent was a good enhancement of sensitivity but cannot be used for solvent extraction.

It was found that aliphatic hydrocarbons cause too much absorption of radiation to be suitable for reliable determination, aromatic hydrocarbons can be used if low fuel flow rates are maintained.

A good enhancement of (Ga) sensitivity is obtained using aromatic hydro carbons, ether and ketone, but standard organic solutions of (Ge) using aliphatic hydrocarbons, like n- butyl acetate, 2- octanone and other ketone. Enhancement for silver (Ag) are highest with aqueous solution and aldehyde solution. Aromatic hydrocarbons and ketone give the best enhancement of (Cu) sensitivity.

The optimum PH of extraction for each extraction system were carried out at varying PH values. The absorbance values for the organic extracts were measured on the atomic absorption instrument . The concentration of metal in the organic extrats was determined by comparison of absorbance values for the extracts with those of standard solutions of the metal in the appropriate organic solvent. From these data, a percent extraction Vs – PH plot was made (Fig1-4).

Table (4) The results of two complexing agent and six solvents were used to Cu extract in (25ml) of organic (solvent)

No.	Solvent	Complexing agent	Maximum absorbance	PH-range	Extraction percent
1-	Butyl ether	Cupferon DEDC	0.43 0.51	2.8-7.6 1.7-6.8	98.9% 99.6%
2-	Butyl acetate	Cupferon DEDC	0.521 0.498	3.8-8.2 2.7-5.3	99.8% 97.9%
3-	Toluene	Cupferon DEDC	0.47 0.49	4-8.5 6.2-8.0	99.99% 97.6%
4-	2- heptanone	Cupferon DEDC	0.52 0.46	2.5-5.2 0.9-2.2	99.2% 82.6%
5-	Isopropyl acetate	Cupferon DEDC	0.59 0.63	2.5-4.6 3.1-5.2	99.8% 97.7%
6-	Butyraldehyde	Cupferon DEDC	0.54 0.45	3.6-5.3 1.5-3.9	97.6% 89.5%

Table (5) Extraction percent vs-PH for (Ag , Ga , Ge , and Cu)

Ag		**Ga**		**Ge**		**Cu**	
PH	**% Extraction**	**PH**	**% Extraction**	**PH**	**% Extraction**	**PH**	**% Extraction**
5	18.6	1	35.24	1	31.65	3	28.6
6	25.2	2	48.4	2	50.09	4	51.2
7	42.4	3	68.9	3	72.41	5	82.05
8	53.5	4	88.22	4	92.3	6	99.01
9	76.4	5	96.3	5	98.7	7	99.85
10	92.4	6	96.28	6	98.7	8	99.86
11	98.4	7	94.01	7	70.15	9	99.85
12	98.38	8	62.3	8	65.02	10	90.11
13	98.4						

Table (6) Enhancement Values with Various Solvents.

No.	**Solvent**	**Enhancement (Ao / Aaq)**			
		Ag	**Ga**	**Ge**	**Cu**
1-	n-Butyl ether	1.45	1.62	1.31	1.6
2-	Nitrobenzene	1.75	1.62	1.53	_____
3-	Cyclohexanol	2.03	1.7	2.01	1.6
4-	Methyl benzoate	2.01	1.8	1.62	1.45
5-	2- Heptanone	1.4	_____	1.6	1.8

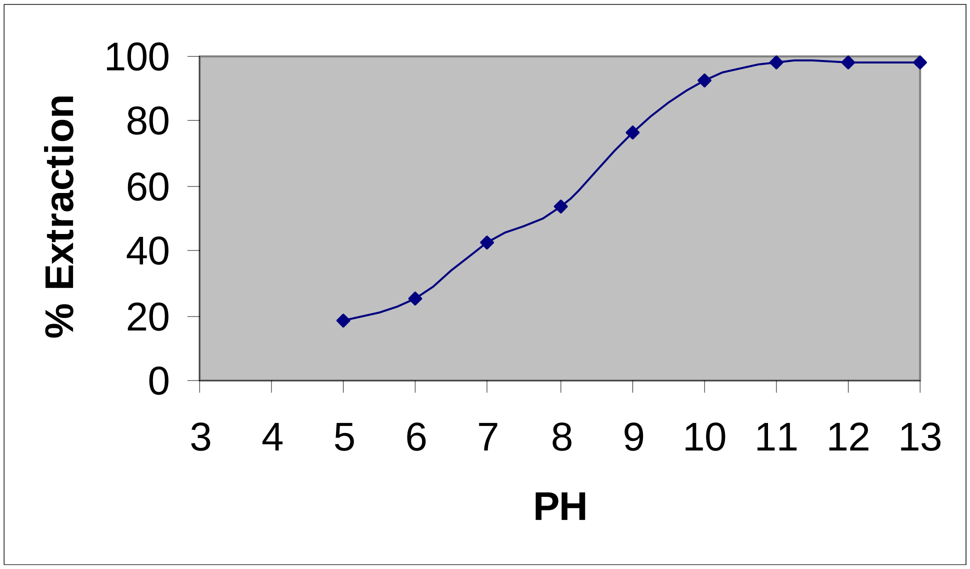

Fig (1) : Percent extraction vs. PH curve for (Ga) using n- butyl ether-DEDC system

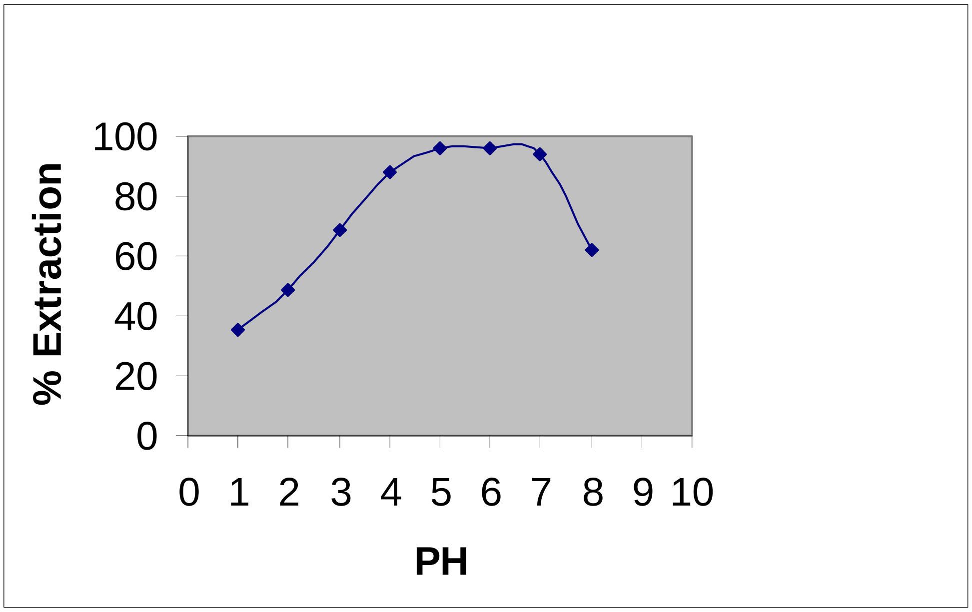

Fig (2) : Percent extraction vs. PH curve for (Ge) using 2- octanone-butyraldehyde system

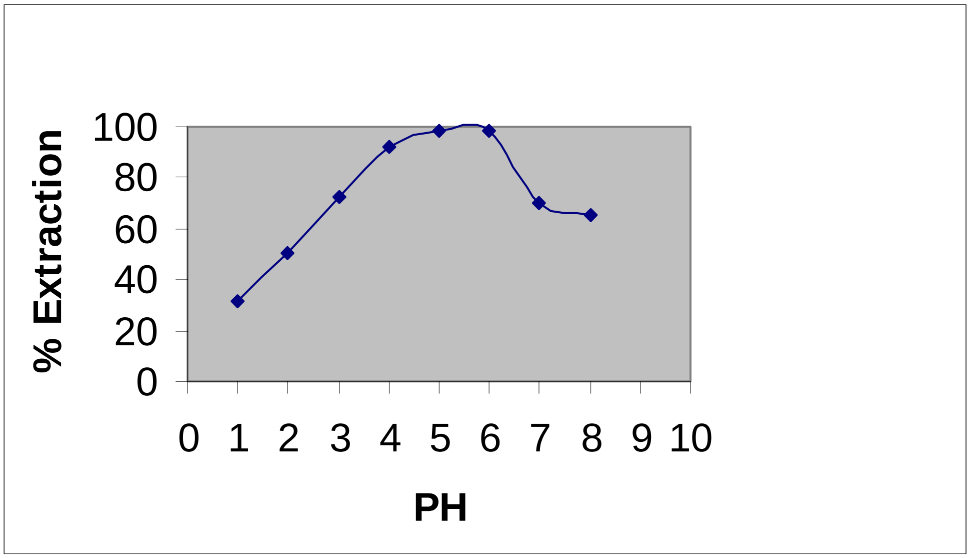

Fig (3) : Percent extraction vs. PH curve for (Ag) using butyraldehyde -cuoferon system

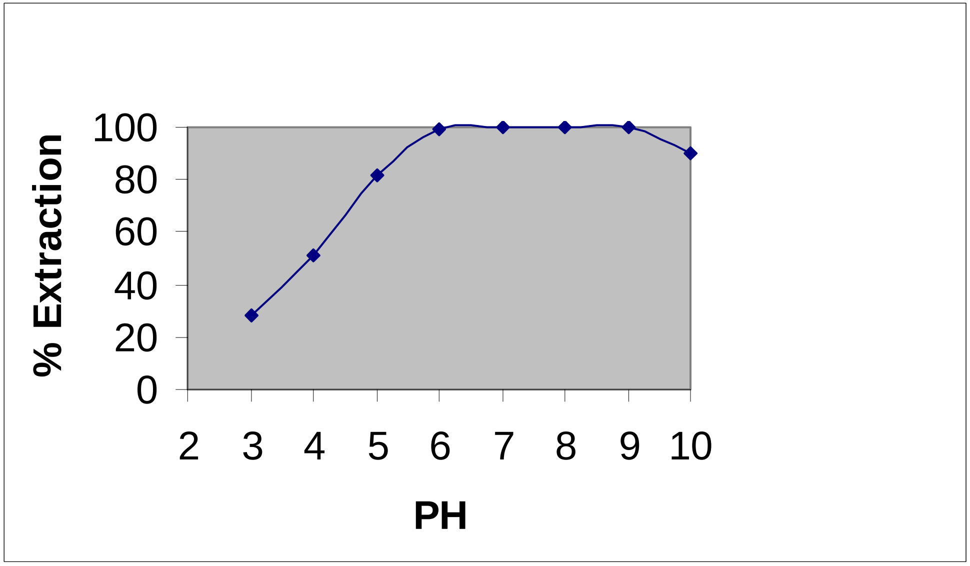

Fig (4) : Percent extraction vs. PH curve for (Cu) using Toluene - cuoferon system

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