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Analytical Solvent Sublation of Metallic Dithizonates

Part I. Solvent Sublation of Copper

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The analytical applicability of the solvent sublation technique was investigated in connection with the separation and pre-concentration of trace metals combined in the form of dithizonates. Sodium lauryl sulphate was used as a collector in connection with dithizone solutions in isobutyl methyl ketone. Under suitable experimental conditions the process allows for the quantitative separation of trace amounts of copper through the easy handling of large liquid samples of up to several litres. Several experimental parameters were studied and optimised including pH, co-ligand to collector ratio and flow-rate of carrier gas. The influence of background salinity was also studied.

Keywords: *Solvent sublation; trace pre-concentration; copper dithizonate separation; water analysis*

The solvent sublation technique is a flotation process by means of which the material adsorbed on the surface of gas bubbles is collected on a layer of immiscible liquid instead of in the form of a layer of foam over a liquid aqueous phase. The technique was proposed by Sebba[1,2] as an alternative for the solution of the problem posed by the formation of persistent foam in ion-flotation techniques. Only a few workers have so far considered the mechanisms and applicability of this technique,[3–10] with no work after 1970, and, as a result, the literature in this field is very scarce and the analytical prospects of the technique remain virtually unexplored.

There are a number of features that make this technique especially attractive from an analytical point of view[7]:

(a) The possibility of easy handling of large volumes of aqueous samples, whereby the concentration factors can easily exceed ratios of 100:1, thus making the technique of great potential interest for the analysis of natural, residual and marine waters for trace elements.

(b) The active material is carried by the gas bubbles and goes into the upper immiscible liquid layer without bringing about mixing of the aqueous and organic phases, so that the separation process can offer high selectivity, potentially greater than that of other flotation techniques. On the other hand, as a minimum fraction of the aqueous phase comes into contact with the organic phase, the solvent sublation technique exhibits greater selectivity than solvent extraction processes. However, the main difference between these processes is that in solvent extraction thermodynamic parameters controlling the extent of extraction can be defined from the establishment of an equilibrium state. In solvent sublation this equilibrium state cannot be established in the bulk of the system but only at the aqueous - organic interface, which can remain virtually immobilised when the gas flow-rate is kept sufficiently low. As a result, as the solvent sublation process is not limited by an equilibrium constant, the recovery of trace elements can eventually reach 100%.

(c) In addition, the phase stirring process associated with liquid - liquid extraction frequently leads to the formation of undesirable emulsions, especially when surface-active species have to be extracted, whereas in solvent sublation processes emulsion formation is negligible owing to the absence of phase mixing processes.

(d) On the basis of similar arguments, the extent of recovery in extraction processes is dependent on the organic to aqueous phase volume ratio whereas solvent sublation is independent of this ratio.

As concluded by Karger,[7] solvent extraction processes pose a number of practical problems when dealing with large volumes of samples, and great potential advantages might therefore result from solvent sublation processes for trace element pre-concentration purposes as it is much less dependent on such limitations.

Dithizone (diphenylthiocarbazone) has been used with good results by Hiraide and Mizuike[11] in precipitate flotation processes, although not in connection with genuine solvent sublation processes. As a result, we initiated a series of experiments in order to establish the possible analytical applications of solvent sublation processes, considering first the use of dithizone as a chelating agent,[12] concentrating our attention in this preliminary investigation on the separation and pre-concentration of trace amounts of copper(II) from solutions of low, medium and high salinity (up to values corresponding to those found in sea water). For this purpose, we optimised a number of experimental parameters and the results obtained by the solvent sublation process were compared with those from the corresponding solvent extraction process carried out under similar experimental conditions.

Experimental

Reagents

All reagents and solvents were of analytical-reagent grade and were used without further purification. The solutions were diluted as necessary to prepare working standard solutions.

Copper stock solution, 1000 p.p.m.

Sodium lauryl sulphate (NaLS) standard solution, 0.01 M.

Dithizone in isobutyl methyl ketone (IBMK) stock solution, 0.324 g l^{-1}.

Apparatus

The experimental device used (Fig. 1) has been described elsewhere[13] and was kept unmodified for this work except for the attachment of a water-cooled glass reflux condenser of high efficiency on the upper part of the flotation column to prevent evaporation losses from the upper organic layer, which was important in long-duration experiments (more than 1 h).

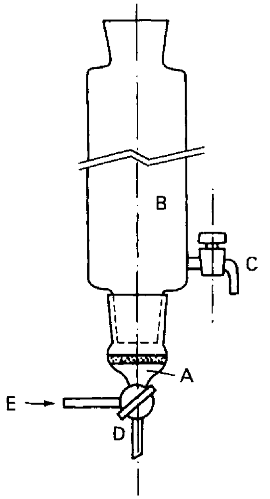

Fig. 1. Experimental device used for the solvent sublation process. A, Detachable section with sintered-glass plate; B, variable size column; C, stopcock; D, three-way stopcock; and E, gas inlet.

An air stream was used as the carrier gas, pre-saturated with water vapour, using a membrane pump and the flow was regulated by means of a needle valve. The gas flow-rate was controlled by means of a bubble rotameter.

The determinations of the residual copper(II) concentration in the aqueous layer during the sublation process were performed by means of a Pye Unicam SP 9800 atomic-absorption spectrophotometer using an air - acetylene flame.

Procedure

All the experiments were carried out using a device that allowed one to treat about 1 l of the aqueous phase, and the initial copper(II) concentration (about 1 p.p.m.) was adjusted before starting the experiments. Suitable amounts of 0.01 M NaLS solution and ethanol were added to the copper(II) solutions and pH adjustment was carried out by means of the necessary amounts of hydrochloric acid or sodium hydroxide solution. Upon transfer of the adjusted solutions into the flotation column, 25 ml of dithizone in IBMK solution were carefully added to the aqueous layer (avoiding mixing of the phases) before the solvent sublation process was started.

Samples of the aqueous phase were taken periodically for analytical monitoring of the process by means of the stopcock attached to the lower part of the flotation device (Fig. 1, C). Upon acidification, when needed, the samples were injected in an atomic-absorption spectrophotometer to determine the residual copper(II) concentration in the aqueous phase, by using calibration graphs prepared with standard copper samples using the same experimental conditions (detergent concentration, ethanol, pH, salinity).

Results and Discussion

Operating Conditions and Flow-rate of Carrier Gas

As a rule it is desirable to work under conditions of maximum specific surface area established between the gas and aqueous phases in order to increase the efficiency of sublate adsorption. Such a requirement can be achieved by means of porous fine sintered-glass plates (No. 3 or 4) aided by the addition of small amounts of ethanol (about 1%) to effect a decrease in the surface tension of the aqueous phase, in order to reduce the size of the gas bubbles passing through the solution. Care should be taken, however, to avoid the addition of excess of ethanol as this would result in a decrease in the yield of the process owing to competitive effects with the sublate for the bubble surface. A similar effect is obtained when the aqueous phase becomes saturated with the organic phase prior to the beginning of the sublation process[5,14]; for this reason such a risk should be avoided by careful addition of the organic phase to the aqueous column.

The column used for our experiments had a capacity of about 3.5 l and a cross-section of 70 cm^2, and was fitted at the lower end with a detachable section furnished with a sintered-glass plate of low porosity (No. 3).

The optimum flow-rate of carrier gas (air pre-saturated with water vapour to minimise carriage of vapour from the aqueous phase by the ascending gas bubbles) was established through a series of preliminary experiments aimed at obtaining a limiting flow value that could guarantee the absence of phase mixing and violent disruption of the organic upper layer. As a result, an upper limit of 80 ml min^{-1} was finally adopted. The optimum flow-rate of the carrier gas depends on a number of parameters directly related to the porosity and mechanical quality of the sintered-glass plate used, to the column size (especially its cross-section) and to the salinity of the aqueous phase (an increase of which favours mixing of the two phases).

The kinetics of the sublation process are obviously a function of the gas - liquid interface generated in unit time as derived from the process mechanism[3–7] and, as a result, both the kinetic features and the process yield will depend on the established gas flow-rate, assuming the gas bubbles to be small enough and of uniform size. In any event, the optimum gas flow-rate will correspond to the maximum flow that will be compatible with the absence of phase mixing and alteration of the upper organic phase, as in the opposite instance the process departs from genuine solvent sublation, approaching, at least partially, a solvent extraction process of lower separation efficiency, as will be discussed further.

Further, as the dependence of the process on the gas flow-rate may be critical, care should be taken to keep the flow-rate reasonably constant, which is fairly easy as the samples to be taken from the aqueous phase during the process are small enough not to bring about a significant variation in flow-rate owing to the resulting charge losses of the liquid column, which produce slight increases in the flow-rate.

Under the experimental conditions used, the total decrease in height of the aqueous phase column arising from the periodic extraction of samples for analysis did not exceed about 3%

of the initial height, thus making it unnecessary to make flow corrections following removal of samples for analytical monitoring.

Attention must be paid, however, to the eventual transport of organic phase by the gas bubbles, which might reach a considerable extent owing to the small volume of organic phase used (25 ml), especially when the process is run for long periods (up to several hours). This problem can be greatly reduced by attaching a suitable water-cooled glass condenser of high efficiency to the upper end of the column,[13] combined with the use of organic solvents of low volatility (IBMK, octan-2-ol, etc.). Provided that the experiments are carried out within a reasonable time (about 1 h or less) there is no need to take special precautions with the dithizone solutions, although it is easy to isolate the system from heat and light.

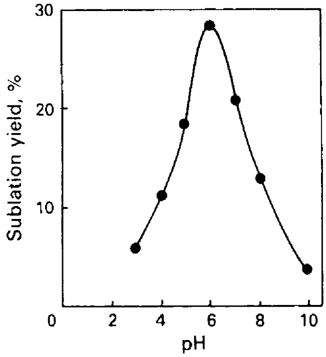

Fig. 2. Effect of pH on solvent sublation yield [NaLS: Cu(II) ratio, 1:1; carrier gas flow-rate, 38 ± 2 ml min^{-1}].

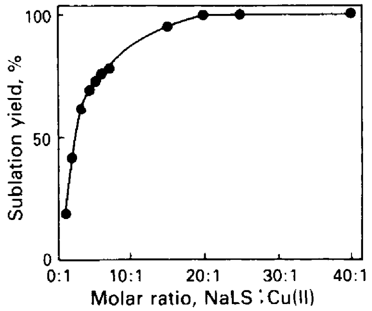

Fig. 3. Effect of NaLS:Cu(II) ratio on the solvent sublation yield (pH, 6.0 ± 0.1; carrier gas flow-rate, 45 ± 2 ml min^{-1}).

Influence of pH

The study of the influence of the pH of the aqueous phase on the process yield was carried out initially keeping a constant NaLS to Cu(II) molar ratio of 1:1, the pH being adjusted by suitable additions of hydrochloric acid or sodium hydroxide solution. Fig. 2 shows the results of these experiments (in all instances the gas flow-rate was kept constant at 38 ± 2 ml min^{-1}), which allows the conclusion that a maximum yield can be obtained only within a narrow pH range near pH 6, the yields being insignificant below pH 3 and above pH 10 (partial decomposition of dithizone was also observed at this pH).

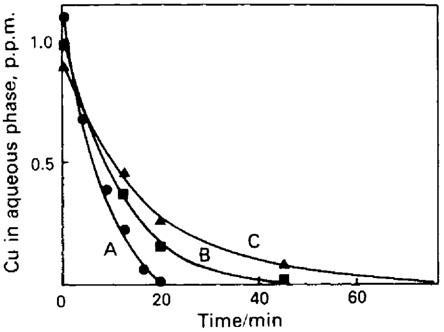

Fig. 4. Effect of NaLS:Cu(II) ratio on the kinetics of the sublation process. NaLS:Cu(II) ratio: A, 40:1; B, 25:1; and C, 20:1.

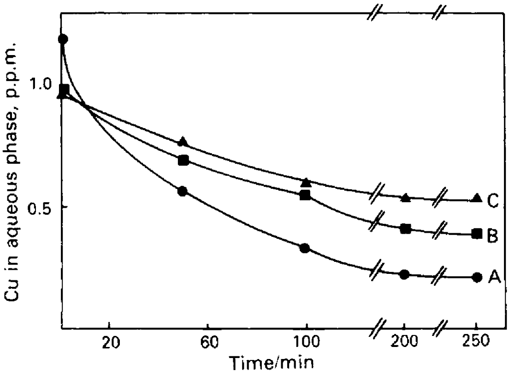

Fig. 5. Effect of salinity on the kinetics and yield of the sublation process. A, 0.5%, gas flow-rate 52 ml min^{-1}; B, 1%, gas flow-rate 50 ml min^{-1}; and C, 3.5%, gas flow-rate 12 ml min^{-1}.

Influence of Surfactant Concentration

A series of experiments were carried out using solutions of pH 6 ± 0.1 with different NaLS to Cu(II) molar ratios while keeping the gas flow-rate constant at 45 ± 2 ml min^{-1}. Fig. 3 shows that the process yield was 100% for ratios of 20:1 or greater. On the other hand, the process kinetics can be studied through the analytical data for the residual content of copper(II) in the aqueous phase obtained from samples taken from the aqueous phase during the process. Fig. 4 shows the kinetic curves obtained for NaLS to Cu(II) ratios of 20:1, 25:1 and 40:1, indicating that under constant gas flow conditions the sublation kinetics increase with increasing proportion of surfactant. However, when a 100:1 ratio is exceeded the process kinetics do not improve any further; on the contrary, the sublation yield decreases, possibly owing to adsorption of the sublate and the excess of free detergent on the gas bubbles.[6]

On conclusion of the process corresponding to a 15:1 ratio, the column contents were vigorously stirred in order to approach extraction equilibrium between the aqueous and organic phases and the copper(II) concentration in the aqueous phase was determined after 24 h of phase settling (complete de-mixing). The extraction yield obtained under such conditions was 75.4%, compared with 96.6% obtained for the solvent sublation process, thereby demonstrating clearly that the solvent sublation mechanism differs from that of liquid - liquid extraction.

In order to obtain more accurate results for comparative purposes, a separate extraction process was carried out using 250-ml extraction funnels and keeping the same organic to aqueous layer volume ratios used in the column experiment. The kinetics and yields of the corresponding processes using in all instances an initial copper(II) concentration of 1 p.p.m. are compared in Table I, which demonstrates clearly the differences between the two processes and outstanding concentration features exhibited by the solvent sublation process.

TABLE I

COMPARATIVE RESULTS OF COPPER(II): DITHIZONE SOLVENT SUBLATION AND SOLVENT EXTRACTION OBTAINED UNDER THE SAME EXPERIMENTAL CONDITIONS

		Solvent extraction		Solvent sublation	
Experiment No.	NaLS:Cu(II) molar ratio	Extraction, %	Time to reach equilibrium/min	Yield, %	Time necessary/min
1	40:1	73.8	~30	100	~20
2	15:1	75.6	~20	95.6	~45
3	7:1	78.4	<8	78.3	—*
4	1:1	78.2	<2	28.4	—*
5	0:1	78.5	<1	—	—

* Yield obtained after 60 min.

Influence of Salinity

As one of the main purposes of this investigation was the application of solvent sublation to the analysis of trace metals in sea water, the influence of salinity was investigated using synthetic solutions of increasing salinity (up to 3.5%). The experiments were carried out at pH 6 starting with an NaLS to Cu(II) ratio of 40:1. Fig. 5 shows the kinetics of the sublation process for different salinities with an indication of the gas flow-rate maintained in each instance. A remarkable kinetic decrease can be clearly observed as the salinity increases, giving rise to a corresponding decrease in yield for a number of pre-set times. Such a result would be expected to occur to a certain extent as the mechanism governing the transfer of the species ascending to the aqueous - organic interface is a process of ionic flotation.[1,15] For saline concentration approaching 3.5% a white turbidity was observed initially, which can be ascribed to the possible precipitation of the surfactant added in considerable concentrations although the turbidity phenomenon was shown to disappear about 10 min after starting the sublation process. The formation of large amounts of froth was additionally observed at the time of introduction of the aqueous phase into the column, which disappeared upon introduction of the organic layer; however, when the process was started the air bubbles were shown to give rise to the formation of a thin layer of froth over the organic phase.

Salt addition results in a change in the interfacial tension, thereby facilitating mixing of the phases, which becomes greater the greater is the salinity. As a consequence, the gas flow-rate had to be reduced to 18 ml min^{-1} at 3.5% salinity in order to prevent phase mixing. In addition, a further decrease in the interfacial tension seemed to occur during the process, which made it essential to reduce the flow-rate to about 12 ml min^{-1} after 100 min. On the other hand, the long duration of this kind of experiment was associated with significant evaporation of the organic solvent.

A final set of experiments was carried out keeping the salinity constant at 3.5% using different detergent to Cu(II) ratios (from 15:1 to 100:1), and it was concluded that either the kinetic features or the process yields could not be improved while it could be easily established that the froth layer settling above the organic phase increased considerably at ratios higher than 40:1. As a result, it was concluded that the investigated system is unsuitable for the pre-concentration of trace metals from high-salinity solutions.

Conclusions

The solvent sublation technique allows a highly effective separation and pre-concentration of trace amounts of copper from aqueous solutions as the dithizonate within a narrow pH range. The yield of the process is 100%, reaching this value for NaLS to Cu(II) ratios greater than 20:1 in not more than 20 min. The efficiency of the investigated sublation process has been shown to decrease sharply as the background salinity of the solution increases.

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