Mines Branch Information Circular IC 284

ANALYTICAL METHODS IN SOLVENT EXTRACTION PROCESSING

by

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ABSTRACT

Analytical methods for the analysis of both aqueous and organic streams in solvent extraction processes are reviewed, especially with reference to the determination of the organic components of these streams. The determination of metals is considered only briefly.

Procedures for the determination of the majority of organic reagents used in commercial solvent extraction operations are given, and areas where methods are required are indicated.

Problems associated with sampling are discussed in some detail.

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Direction des mines
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MÉTHODES ANALYTIQUES DANS LE TRAITEMENT DE L'EXTRACTION AU POLVANT

par

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RÉSUMÉ

On passe en revue les méthodes analytiques pour l'analyse des fluides aqueux et organiques dans les procédés d'extraction au polvant surtout pour déterminer les composantes organiques de ces fluides. La détermination des métaux n'est considérée que très brièvement.

On présente les procédés pour déterminer la majorité des réactifs organiques utilisés dans les opérations commerciales d'extraction au polvant, et on indique les régions où ces methodes sont nécessaires.

On discute en détail les problèms associés à l'échantillonnage.

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INTRODUCTION

Hydrometallurgical processing of ores and allied materials is becoming of particular importance in the mining field. Included in this trend to hydrometallurgy is the use of solvent extraction as a unit process. Considerable interest is presently being directed towards the use of solvent extraction techniques for the separation and recovery of metals from aqueous solutions. This process has been adopted in many plants for the recovery of non-ferrous metals[1], and the nuclear industry continues to expand the use of this technique for the separation and recovery of radioactive products[2].

But while solvent extraction processes continue to be developed, little is apparently being done in the associated field of analytical chemistry. Methods which are available for the determination of solvent components, especially in aqueous raffinates and streams, from solvent extraction processes are scattered throughout the literature. Many solvent extraction processes are in operation, but except for one instance, no references to analytical methods, or accurately determined solvent losses, are given. Indeed, plants have been put into operation without any analytical determination of extractant losses. In many cases suitable analytical methods are just not available. Methods for the determination of all the components of a solvent (extractant, modifier and diluent) in an aqueous raffinate are still required. Most solvent loss figures are determined by inven-

tory. Such a method provides only the total (soluble, entrained and volatile) losses over a period of several months' operations. Day-to-day losses cannot be determined by this approach, which is thus not applicable to the determination of solvent losses from short pilot plant runs.

Solvent loss to waste streams can affect quite seriously the economics of a solvent extraction process, and can also have detrimental effects on the environment. The trend towards the control of pollution of streams by legislative bodies will, sooner or later, require analysis of waste streams for organic materials such as those used in solvent extraction processes.

It has become apparent that a need exists for a comprehensive review of the analytical chemistry associated with the process of solvent extraction. This monograph is an attempt to fill this need.

The main subject of this monograph is the analysis of solvent components in both the aqueous and organic phases. Analytical methods directly or indirectly applicable are reviewed, and appropriate methods are described. Problems associated with the sampling and analysis of solvent extraction streams and solutions are considered in some detail. Areas where analytical methods are required are indicated. Procedures for the determination of metals in the aqueous and organic phases are only briefly considered since many methods and texts are available in this area.

THE SOLVENT EXTRACTION PROCESS

A brief description of the process of solvent extraction will be given here, mainly for reference purposes. More complete descriptions of this process are available elsewhere[4-6]. The nomenclature of solvent extraction, as applied to industrial processes, has been published[7], and should be consulted if necessary.

The process of solvent extraction, as applied generally in the treatment of metal-containing solutions, is shown schematically in Figure 1. The metal-bearing aqueous feed and the solvent are fed, usually in a counter-current manner, into a contactor. In this stage, the metal of interest is transferred from the aqueous to the organic phase, and the raffinate is then treated for the recovery of other metals, recycled to some point upstream or downstream from the solvent extraction process, or goes to waste.

Following extraction of the metal, the loaded solvent leaving the extraction stage may be scrubbed with a suitable aqueous solution. In this stage, small amounts of impurities in the loaded solvent are removed. The scrub raffinate is generally recycled to a stage upstream from the solvent extraction circuit, for example to the leaching stage, or to the solvent extraction feed tank.

After scrubbing, the loaded solvent then passes to a third stage in which the metal is stripped from the organic phase by some suitable aqueous solution, producing a (usually) fairly concentrated solution of the metal salt.

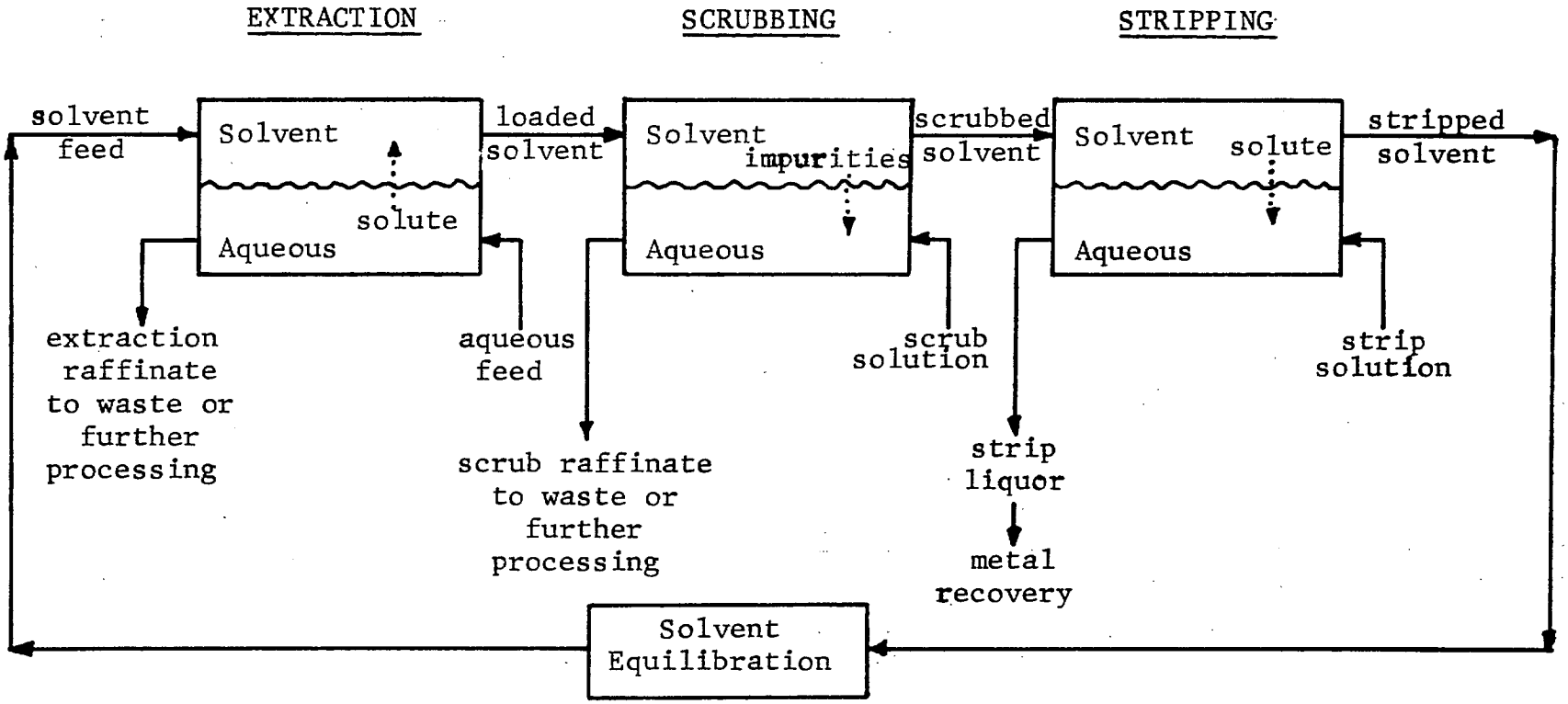


Fig. 1: The Ceneral Process of Solvent Extraction

The stripped solvent is recycled to the extraction stage. If necessary it is treated (equilibrated) prior to entering the extraction stage.

Each of the three stages described above - extraction, scrubbing and stripping - may involve several contactors for each stage. Thus the extraction of uranium from acid sulphate solution, using a tertiary amine as extractant, may require 3 stages (mixer settlers) for extraction, 1 stage for scrubbing, and 2 stages for stripping.

Considering only the solvent extraction process, there are then eight streams of interest: aqueous feed, solvent feed, extraction raffinate, scrub solution, scrub raffinate, strip solution, strip liquor and stripped solvent. All will require chemical analysis for their various components.

Economic and Pollution Considerations

In order to bring solvent losses into perspective, it is constructive to consider both the economics involved and aspects of environmental pollution.

As in any industrial process, economic factors are of prime importance. Thus the use of solvent extraction is predicated on the values of the metals involved compared to the cost of the refining process. Ideally, a solvent extraction process involves a cheap solvent which will selectively and quantitatively extract a metal (or metals) from a given aqueous feed; will not degrade on recycling; have no solubility in the aqueous phase, and is readily

stripped of its metal values. Unfortunately such a process is far from a reality. If solvent losses are very small (a few ppm) and the solvent is stable, the solvent extraction process can be economical. The major costs are then for plant and solvent inventory.

Solvent loss figures that are presently available from various plants are given in Table 1. The majority of these figures are calculated from inventory. Only in one case is any distinction made between losses due to solubility and degradation. It might be pointed out here that solvent that is entrained or soluble in raffinates represents potentially recoverable solvent, either by mechanical means such as settlers or filters, or by adsorption onto an activated solid such as carbon. Loss of solvent by volatilisation may be considered as none recoverable.

It is evident from Table 1 that solvent losses can play an important role in determining whether a particular process is economically attractive.

The other major concern associated with solvent losses is that of pollution. It is known that small amounts of some organic compounds are toxic to fishes[8]. Large solvent losses can also result in oil-like films on the surfaces of streams and lakes. While the effects of solvent extraction reagents on fish and other life has not yet been studied, the growth of solvent extraction plants will undoubtably warrant investigations into such factors.

TABLE 1

Solvent Losses Reported for Some Processes

Metal Extracted	Extractant	Extraction pH	Solvent loss ppm	References
Ni	Naphthenic acid	4.0	90	9
	Naphthenic acid	6.5	900	10
	Versatic 911	7.0	900 600	11 Shell data
Co	Versatic 911	7.7	100	12
Rare Earths	D2EHPA	2.0	7	Private comm.
Co	D2EHPA	5.5-6.5	30	13
U	Tert. Amines	1.5-2.0	10-40	14-17
Cu	LIX-64	1.5-2.0	4-15	18-21
U	TBP	2.0	25-40	22
Cu	Kelex 100	1-2	10	23
Hf	MIBK	1-5 M HCl	20,000	24

If only for these two reasons - economic and environmental - there is sufficient incentive and need for the development of analytical methods to determine small concentrations of solvent components in aqueous waste streams from solvent extraction circuits. Other reasons which may be mentioned are, for example, the effect of organic compounds in the strip liquors which may affect subsequent processing of these liquors; or the degradation of the solvent due to oxidation or attack by acids present in the aqueous feed solutions.

Components of the Solvent

Solvents used in the industrial applications of solvent extraction consist of at least two components. These are: (i) the extractant, the active reagent which complexes with metal ions; and (ii) the diluent, which is usually an "inert" organic hydrocarbon. Generally a diluent is considered not to take part in the extraction, and is added only to modify the physical characteristics of the extractant. Many of the so-called inert diluents do, however, have some effect on the extraction of metals[25].

A number of solvent systems also require the addition of a modifier, an organic compound added to reduce or eliminate the formation of a third phase, an emulsion, or both. Ideally, all three components would be insoluble in an aqueous solution, but since this is not possible, those with a minimum solubility are favored for industrial use.

(I) EXTRACTANTS

There are essentially four classes of extractants presently in use, or proposed for use, in solvent extraction plants. These are given in Table 2, and are the ones of concern in this monograph. A brief description of each class follows.

(i) Acidic Extractants

The most versatile of this class of extractants is di-(2-ethylhexyl) phosphoric acid (D2EHPA). This reagent has been used for the extraction (or separation) of such metals as Al[59]; Be[60]; Ca, Sr[61]; Co, Ni[13]; Cu[45]; Ga[62]; Mn[63]; U[41]; Th[64]; V[65]; and rare earths[66]. This extractant is, as are others of this group such as carboxylic and sulphonic acids, a liquid cation exchanger. Extraction of a metal ion may be written, in its simplest form:

$$M^{n+} + \overline{n(RO)_2PO(OH)} \rightleftharpoons \overline{((RO)_2POO)_nM} + nH^+ \qquad [1]$$

where the bar represents the organic phase. For the case of the extraction of cobalt, the extraction conforms to the following stoichiometry -

$$CoSO_4 + \overline{2(RO)_2PO(OH)} \rightleftharpoons \overline{((RO)_2POO)_2Co} + H_2SO_4 \qquad [2]$$

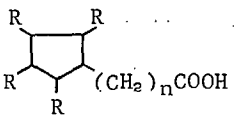
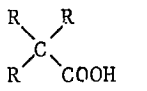
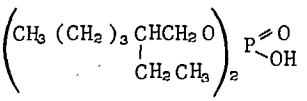
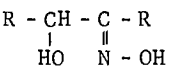
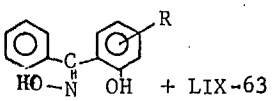
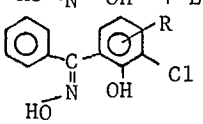
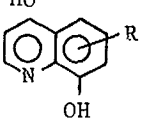
Similar equations can be written for other liquid cation exchangers.

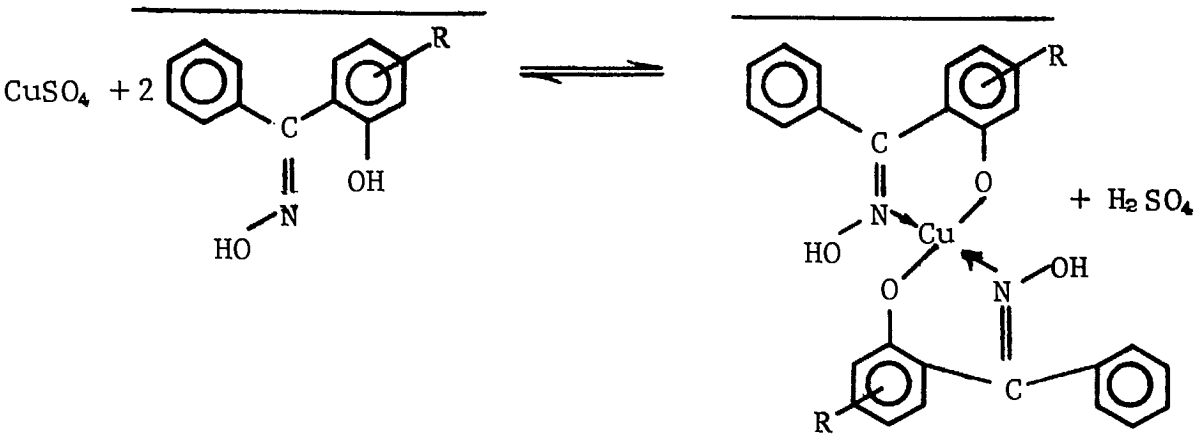
(ii) Chelating Extractants

This class comprises the most specific of the commercially available extractants. These reagents form chelate complexes with metal ions. Thus LIX-64N (a General Mills product) forms a chelate with copper in acid solution according to the equation:

TABLE 2

Commercially Available Extractants

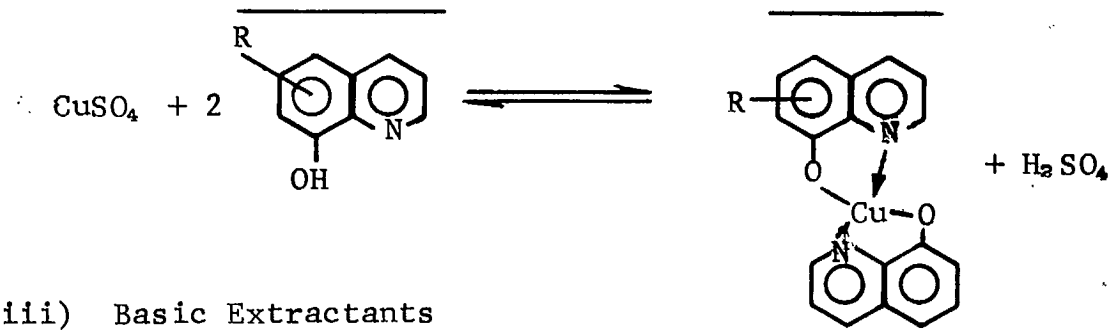
Extractant	Type	Structure	Supplier	References to uses
Tri-n-butyl phosphate (TBP)	Neutral or Solvating Extractants	$(CH_3CH_2CH_2CH_2O)P{=}O$	Ashland Chemicals	26-32
Methyl isobutyl ketone		$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	Ashland Chemicals	33-35
Alcohols (various)		--	--	36-38
Naphthenic acids	Acidic Extractants		Shell Chemicals	39
Versatic acids			Shell Chemicals	39
Di(2-ethylhexyl)-phosphoric acid (D2EHPA)			Union Carbide	13,40-44
LIX-63 (Not now available)	Chelating Extractants		General Mills Inc.	45,46
LIX-64N			General Mills Inc.	18-21,47-50
LIX-70			General Mills Inc.	51
Kelex 100 and 120			Ashland Chemicals	23
Media I and II		?	Ashland Chemicals	--
Primary amines	Basic Extractants	RNH_2 $R=C_{12}-C_{14}$	Rohm and Haas	42,52,53
Secondary amines		R_2NH N-lauryl trialkyl methyl amine	Rohm and Haas	54,55
Tertiary amines		R_3N $R = C_8 - C_{10}$	General Mills Inc.	14-17,56,57
Quat. Amm. Salts		$(R_3N^+CH_3)Cl^-$ $R = C_8 - C_{10}$	Ashland Chemicals	43,58



[3]

This reagent is being used successfully in several commercial plants for the extraction of copper from dilute copper sulphate leach solutions[18-21].

Other commercially available chelating extractants are those produced by Ashland Chemicals under the names Kelex 100 and 120. These are substituted 8-hydroxyquinolines, which are presently being piloted for the extraction of copper from dilute acid solutions.



(iii) Basic Extractants

Commercial extractants in this class are limited to long chain aliphatic amines. All four types, primary, secondary, tertiary and quaternary are, or have been, used for the solvent extraction of metals. The usefulness of these anionic liquid ion-exchangers is dependent on the ability of a metal to form

an anionic specie in the aqueous phase. For example, species such as $CoCl_4^{2-}$, $FeCl_4^-$, $CuCl_4^=$, $UO_2(SO_4)_2^{2-}$ can be formed, and are extracted by amines. A general equation for extraction of metals using a tertiary amine is:

$$MA_m^{(n-m)} + \overline{(m-n)R_3NHA} \rightleftharpoons \overline{(R_3NH)_{m-n}MA_n} + (m-n)A^- \qquad [5]$$

As an example, uranium as the anionic uranyl sulphate is extracted by a tertiary amine, such as Alamine 336, according to equation 6.

$$UO_2(SO_4)_2^{2-} + \overline{(R_3NH)_2SO_4} \rightleftharpoons \overline{(R_3NH)_2UO_2(SO_4)_2} + SO_4^{2-} \qquad [6]$$

In most cases, pre-equilibration of the solvent (amine) must be carried out. In the case of uranium, this is done by contacting the solvent with a dilute sulphuric acid solution to form the amine sulphate in the organic phase -

$$2R_3N + H_2SO_4 \rightleftharpoons (R_3NH)_2SO_4 \qquad [7]$$

Amines have been used mainly for the extraction of U[14-17], Co[56,57], Mo[67], rare earths[52] and Th[53].

(iv) Neutral Extractants

The most prominent extractant in this group is undoubtably tri-n-butyl phosphate (TBP). This can be used in concentrations up to 100%, but is usually employed as a 25 - 50 vol.% solution in a diluent such as kerosene. It is used mainly in the refining of uranium[29] and in the nuclear field for the separation and purification of radioactive metals[26], usually from nitrate or nitric acid solutions.

While TBP has enjoyed particular success as an extractant,

the mechanisms of extraction of metals, the degradation of TBP, and the formation of non-strippable complexes, is still not completely understood[29]. For the extraction of a metal from, for example, a nitrate system into TBP, a general mechanism may be written as:

$$M^{n+} + nNO_3^- + \overline{(a - bc)H_2O} + \overline{bTBP(H_2O)_c} \rightleftharpoons \overline{M(NO_3)_n(H_2O)_a(TBP)_b} \quad [8]$$

where $(a - bc)H_2O$ is the water taken up by the extractant; $bTBP(H_2O)$ is the hydrated extractant, and $M(NO_3)_n(H_2O)_a(TBP)_b$ is the extracted metal specie.

(II) DILUENTS

A diluent may be defined as the organic liquid in which an extractant (and modifier if necessary) is dissolved to produce a solvent. The diluent is usually the major component of the solvent.

Typical of the diluents used, or available, commercially are those given in Table 3. For all analytical purposes, diluents may be considered as being inert, and hence present a considerable problem in their determination in small amounts in aqueous solution, especially in the presence of the other components of a solvent.

(III) MODIFIERS

These are reagents added to a solvent to inhibit the formation of a third phase, and also to inhibit emulsion formation. In industrial practice modifiers are limited to isodecanol, 2-ethylhexanol and TBP. The concentration of modifier may be as

TABLE 3

Some Commercially Available Diluents

Diluents	Sp. Gr. 20°C	Initial B. Pt. °F	Flash Pt. °F (TCC)	Type
Benzene[a]	0.883	176	5	Aromatic
Toluene[b]	0.873	230	44	Aromatic
Xylene[b]	0.870	281	80	Aromatic
Solvesso 100[b]	0.876	315	112	Aromatic
Solvesso 150[b]	0.981	370	151	Aromatic
Iosol 2429[b]	0.760	240	54	Paraffins + Naphthenes
Varsol DX3641[b]	0.793	361	135	+ Aromatics
Mineral Spirits[a]	0.786	315	105	Aliphatic
Odorless 360[a]	0.761	351	123	Aliphatic
140 Flash Naphtha[c]	0.785	364	141	Aliphatic + 10% Aromatic
Mineral Spirits[d]	0.784	310	104	Aliphatic +
Odorless Min. Sp.[d]	0.757	352	128	Naphthenes
Isopar L[b]	0.767	373	144	Paraffins 93%; Naphthenes 7%
Napoleum 470[e]	0.811	410	175	Aliphatic

[a]Ashland Chemical. [b]Imperial Oil. [c]Shell Chemicals. [d]Amsco. [e]Kerr-McGee.

high as 20 vol.% in solvents containing high concentrations of amines, but is usually around 2 - 5 vol.% of the solvent. Some physical properties of these reagents are given in Table 4.

REAGENT SOLUBILITY

In all cases where two 'immiscible' liquid phases are contacted there will be a certain solubility of one phase in the other. Thus, in solvent extraction processes the aqueous raffinates will always contain some of the organic phase. Two main causes of solvent loss to the aqueous phase can be distinguished; (i) chemical loss or solubility of the components of the organic phase in the aqueous phase, and (ii) physical loss or entrainment of discrete droplets of the organic phase in the aqueous phase. In a solvent-in-pulp (SIP) process[78], a further cause of solvent loss to the raffinate is sorption of solvent on the solid particles of the slurry.

(i) Solubility of the Organic Phase in the Aqueous Phase

Solubility of solvent in the aqueous phase will always occur in liquid-liquid extraction to some extent. Theoretically, at least two main reasons for this can be distinguished. One is the solubility of the solvent components, the other the solubility of the metal-extractant complex in the aqueous phase. These two cases are shown schematically in Figure 2, where the basic equilibra established in a simple extraction process are illustrated.

TABLE 4

Modifiers

	Sp. Gr.	B. Pt. °F	Flash Pt. °F (TOC)
2-ethylhexanol[a]	0.834	365	185
Isodecanol[a]	0.840	428	220
Tri-n-butyl phosphate[b]	0.973	352	380

[a]Ashland Chemicals

[b]Canada Colors Ltd.

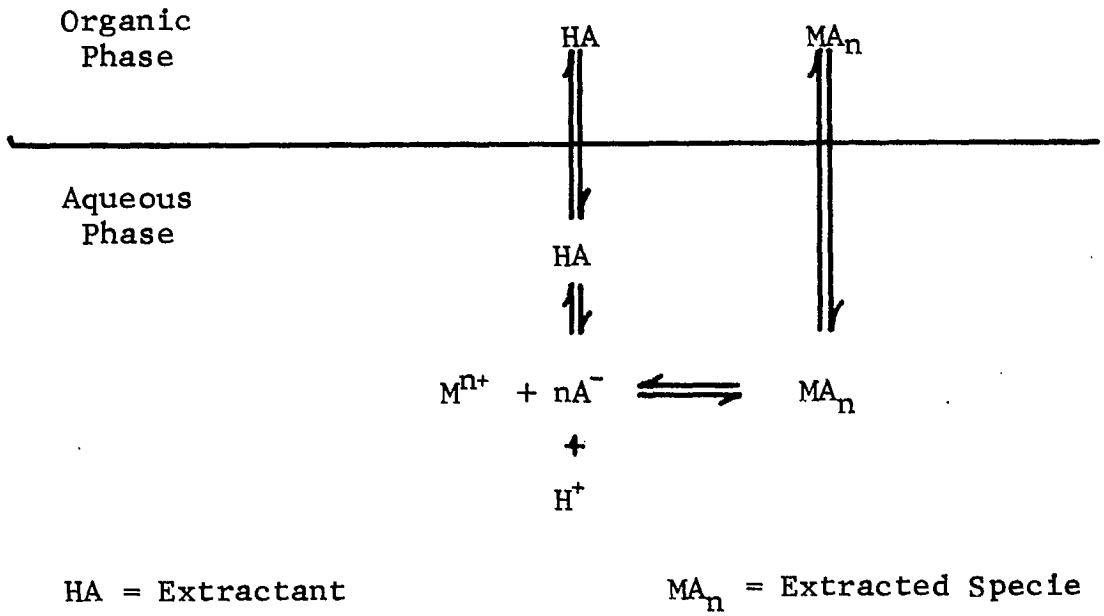


Fig. 2: Some of the Equilibria Involved in the Extraction of a Metal

In the case of acidic, basic and chelating extractants (weak acids or bases), their weak polar character will always result in some solubility in the aqueous phase over the pH range generally useful for solvent extraction processes (pH 1 to 8). The solubility will depend both on the pH and on the salt concentration in the aqueous phase. These two parameters have been illustrated for the case of a tertiary aliphatic carboxylic acid (Versatic 911)[11]. The effect of pH on the solubility of naphthenic acid is also evident from the losses given in Table 1. It is also to be expected that solvent solubility in the aqueous phase will increase with increase in temperature.

Since most solvents are composed of two or three components, it is reasonable to expect some solubility of each component in the aqueous phase. However, it is unlikely that each component of the solvent will have the same solubility. Thus, it is to be expected that the more soluble components (extractant and modifier) will be appreciably more soluble than the diluent, which has no ionisable atoms. There is no evidence in the literature that each solvent component has been determined in an aqueous raffinate.

An indirect cause of extractant solubility in the aqueous phase is due to its degradation. The most thoroughly investigated extractant in this respect is TBP, and considerable data have been reported on this reagent[26]. Generally the degradation products are dibutyl and monobutyl phosphates, which

have substantial solubility in aqueous solution. For this, and other reagents of this type, the determination of extractant in raffinates is complicated by the presence of such degradation products.

(ii) Solubility of the Aqueous Phase in the Organic Phase

The solubility of water in solvents can vary greatly[70]. In pure or undiluted extractants, water solubility is generally much higher than when extractants are dissolved in a diluent. For example, pure di-n-butyl phosphoric acid will dissolve about 100 g of water per liter at 25°C[68,69]. The metal content of the solvent also affects the solubility of water in the solvent. Thus on increasing the sodium salt concentration of di-(2-ethyl-hexyl) phosphoric acid (D2EHPA) in benzene solution, the amount of water taken up by the solvent increases linearly[71].

Increasing the concentration of TBP in a hydrocarbon diluent increases the uptake of water by the solvent when contacted with an aqueous solution. Thus at 20 vol.% TBP in kerosene, the water concentration after contacting with an aqueous solution is about 4 g/l, and at 80 vol.% TBP is about 28 g/l[72], both at 25°C. The solubility of water in most commercial hydrocarbon diluents is low ($\ll 1$ g/l).

The ability of solvents to take up water and water soluble materials such as acids, alkalis, and salts can affect the analytical methods used for the determination of solvent components. Thus, it is important that the analyst be aware of this problem,

and not assume that because the sample is organic in nature that it does not contain water, or other components of the aqueous feed, with which it has been contacted. For example, the presence of a small amount of soluble aqueous acid in an amine-containing solvent would give rise to low results on the determination of the amine by titration with acid.

(iii) Entrainment

Loss of solvent by entrainment in the aqueous phase can result from several causes. For example, the type of contactor used, the amount of agitation in the contactor, settling rates of solvent and aqueous phases, emulsion tendencies, third phase formation, temperature, presence of solids in the aqueous phase, and flow rate are typical causes.

Generally, entrained solvent will slowly coalesce on standing, to form a layer on the top of a sample. The rate of appearance of such a layer (or globules) of solvent will depend on several factors, one of which is the size of entrained droplets. This can present the analyst with considerable problems. It may not be visually evident that entrained solvent is present in in an aqueous sample, especially if the sample is colored or turbid. Analysis of such a sample, containing entrained solvent, would give entrained plus soluble solvent. If the sample were allowed to stand for any length of time, most of the entrained solvent could coalesce at the surface and be omitted from an aliquot taken for analysis. In such cases, the analytical results would

depend on the length of time between sampling and analysis.

The analysis of the components of entrained droplets of solvent would probably show them to approach closely the analysis of the bulk solvent, whereas the soluble components in the aqueous solution could be quite different.

(iv) Solvent Volatility

In industrial solvent extraction operations the diluents used have boiling points of the order of 350 - 500°C, and flash points of generally in excess of about 65°C. This is necessary because of safety and insurance requirements.

Losses of diluent (and other solvent components) can, and do, occur as a result of their volatility, especially if the solvent extraction circuit is operated at high temperatures. Diluent losses by volatalisation will result in an increase in the concentration of extractant in the solvent, especially if the loss of extractant to the raffinate is very small. Most extractants are considerably less volatile than the diluents usually used.

Volatile losses could be particularly evident in mixer settler operations where large settler areas are needed for phase disengagement. Most operations of this type employ covered settlers to overcome this type of loss.

SAMPLING

It is a self-evident truth that an analysis is only as good as the sample on which the analysis is performed. In far too many cases this axiom is not known or is ignored, both in sampling in the plant and also in the laboratory. It cannot be stressed too strongly that (usually) a sample is only a representitive of a whole or population, and is not in itself the population.

The degree to which a sample is representative of the population from which it is taken depends, in part, on its size and on the homogeneity of the population. Thus, sample size is an important factor in any sampling scheme, and especially so when the homogeneity of the material being sampled is questionable.

Considerable thought must be given to sampling techniques if the analytical results are to be meaningful. The problem also involves the economics involved, both in sampling and in carrying out the analyses. The more samples which are taken and analysed, the more certain will be the analytical result. But this must be weighed against the costs of taking the sample, and the costs of analysis.

Sampling techniques for many types of materials have been described[73,74], and the statistical approach has been well documented[75]. However, the sampling of the streams in solvent extraction processes involves problems peculiar to such

processes which do not appear to have been detailed in the literature. These are dealt with below, in some detail.

(i) Sampling the Aqueous Phase

As noted earlier, most extractants used in commercial solvent extraction plants are surface active. Consequently, they will be readily sorbed on to the surfaces of sample containers, and this fact must be taken into account in the sampling and analysis of solvent extraction streams.

The effect of surface adsorption will be greatest when only small amounts of solvent are present in the sample. As the solvent concentration decreases the sample taken for analysis usually increases. This requires a larger sample container with a resultant increase in surface area available for adsorption. Problems can also arise in the transfer of aliquots of the sample for analysis. For example, in the determination of small amounts (ppm) of tertiary amine in aqueous solutions, it was found that adsorption of amine on the pipette produced results up to 20% low[117]. This effect was overcome by rinsing the pipette at least five times with the sample solution prior to taking an aliquot for amine determination. Another example of amine adsorption on to container surfaces has been given by Milun and Moyer[77]. They show the loss of amine from an aqueous solution on to polyethylene, and on to Desicote-coated glass containers, as a function of time. This is illustrated in Figure 3 for polyethylene. On glass containers coated with Desicote, very little amine adsorbed.

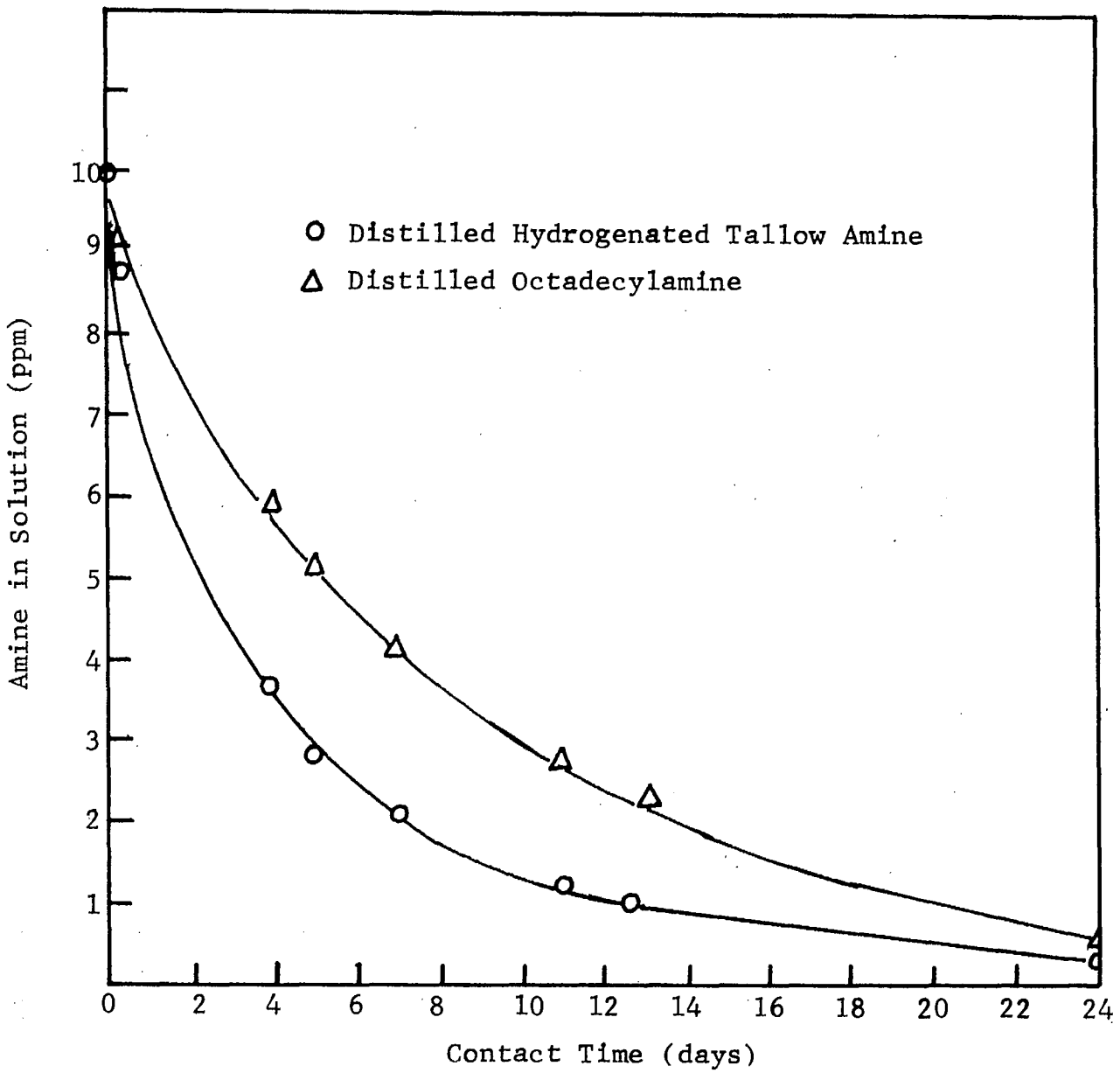


Fig. 3: Adsorption of Amines on to Polyethylene
(from ref. 77)

The problem of adsorption would occur when taking the sample in the plant, thus it is advisable to rinse the sample container several times with the solution being sampled prior to taking a sample for analysis. Specially prepared sample containers could also be used.

It is also evident from Milun and Moyers work that samples should be analysed as soon as possible after they are taken.

To obtain consistent results on samples which contain, or are suspected to contain, entrained solvent, it is preferable to remove this prior to analysis. In cases where inefficient plant operation results in visual amounts of solvent in the aqueous sample, analysis of such would be meaningless. If the soluble portion of the solvent is to be determined, the entrained solvent must be removed. This can be accomplished by separation in a separatory funnel; removing by suction; or by filtering through a coarse, dry filter paper*. The aliquot may also be taken from below the surface by means of a pipette. For the removal of smaller amounts of entrained solvent, filtering through a dry filter paper will provide a solution suitable for analysis.

For the separate determination of soluble and entrained solvent, the following approach is useful, but only when the amount of entrained solvent is small. Shake the sample thoroughly and take an aliquot for analysis, bearing in mind the points discussed above about sorption. Filter the remaining sample several times

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*Some loss of soluble organic material may result from using filter paper.

through dry filter paper, and analyse the filtrate. The difference is due to entrainment. Centrifugation may also be useful for separating entrained solvent.

The size of the sample originally taken from a process stream will be governed by several factors, such as the sensitivity of the methods of analysis, the amount of entrained solvent expected, and the number of analyses to be carried out on the sample. One way of minimising the effects of sorption of solvent on sample containers and pipettes is to make the sample size the same as that required for the analysis. In this way the whole sample is used, and the container can be washed with methanol or other reagent to remove sorbed solvent. If the container is washed with the solution being sampled, this would not be necessary. A drawback to this method of sampling is that the sample taken may not be sufficiently large to be representative of the stream being sampled. It may, therefore, be necessary to make a compromise between sample size and analytical result.

The problem of entrained solvent in an aqueous sample is essentially one of non-homogeneity. To obtain a meaningful analysis, any sample must be homogeneous. Visual amounts of solvent in an aqueous sample, therefore, means that any analyses carried out can provide only approximately true results, and this must be understood by both the analyst and engineer.

(ii) Sampling Slurries

The economic advantages to be gained by application of the so-called solvent-in-pulp process[78] to commercial operation are many. This process involves extraction of a metal from a leach slurry and obviates the need for filtration of the solid material. Several pilot plant studies have been made on this process, with particular successes[79,80]. The contactors used in these studies were sieve-plate pulse columns[78].

Sampling of slurry raffinates presents major problems. The rate at which solids in a slurry settle is dependent on solution viscosity, density and size of the solid particles, temperature, and so on. The greater the settling rate the less chance there is of obtaining a representative sample. In fact, it is doubtful if a truly representative sample from such a stream can be obtained.

The time between sampling and analysis can vary considerably. Ideally, the sample should be analysed almost immediately after sampling. This, unfortunately, is the exception rather than the rule.

There are essentially three points to consider in determining solvent losses is slurries. First, physical entrainment; this is more likely to occur in slurries than in liquid-liquid extraction because the solids can drag solvent into the raffinate sampling port of the contactor. Secondly, sorption of solvent on to the surfaces of the solid particles; this may be considered as

a special type of entrainment, and in fact may give rise to entrainment if the sorption results in small globules of solvent adhering to the solids. Finally, there is the solubility of the solvent in the aqueous phase. And here again, it is expected that loss of the more polar constituents of the solvent will be greater than for the non-polar constituents.

It is probably impossible at this time to determine quickly and accurately these three separate types of solvent loss. Entrainment losses, for example, are not readily obtained by volume measurement because the solids in the sample can trap droplets of solvent as they settle. From observations of slurry raffinate samples, it has been found that droplets of solvent are released from the settled solids over periods of hours and days, and these coalesce on the surface of the aqueous portion of the sample. The problem is not readily solved by agitation of the sample. For example, to agitate the solids so as to maintain them in a suspended state in order that the occluded solvent be freed, requires agitation such that as the solvent is released, it is again dispersed in the suspension. As the solids settle after agitation, the solvent is again trapped. This problem has not, as yet, been solved.

Neglecting the problem described above, analysis of slurry samples can be accomplished in essentially two ways. The first approach is to use the whole sample for the determination. This would provide a total solvent loss. The other approach is to

separate the solid and liquid phases and analyse each separately.

In the former method one major drawback is that, in order for the sample to be in any way representative of the stream being sampled, it has to be larger than the aliquot taken for analysis. The problem then is how to take a representative aliquot from this large sample. In the latter approach, the problems of entrapment of solvent, etc., can be serious and vary from sample to sample. Further, analysis by the second method will take at least twice the time as for the former.

It is evident that the whole problem of sampling aqueous raffinates (liquid and slurry) is complex, and that many compromises may have to be made between the sampling and analytical procedures. Further, analysis of a single sample can provide quite erroneous and misleading results, consequently solvent losses should only be viewed in the light of several analytical determinations.

(iii) Sampling the Organic Phase

Compared to sampling aqueous raffinate streams, the sampling of organic phases is relatively free from problems. Here, the stream is much more homogeneous. The problems are then not so much in sampling the organic streams in the plant, but in sampling in the laboratory.

Loaded solvents, which may contain more than 20 g metal/l, are invariably viscous. This results not only from the metal concentration but also from the fact that relatively high concentrations of extractant are sometimes used to obtain high metal loadings, and

so reduce the solvent throughput in the plant.

In transferring and measuring such solutions by pipette, drainage of the pipette becomes a serious problem. The same situation obtains with aqueous solutions containing high concentrations of salts. One way of circumventing this problem is to use a calibrated pipette, of known total volume, and rinse it with a suitable solvent after transfering the sample. Thus, the sample is transfered quantitatively for analysis.

Aqueous or solid entrainment in organic samples can usually be removed quite readily by contrifugation, or, if the viscosity of the sample is not too high, by filtration through a phase-separating paper such as a Whatman 1PS.

ANALYSIS OF THE ORGANIC PHASE

DETERMINATION OF EXTRACTANTS

Extractants which are considered here are generally those given in Table 2, and are treated in their respective classes. The determination of these reagents in organic (solvent) and aqueous phases are treated separately.

An outline of one or more available methods for each extractant is given, together with any comments which are deemed necessary. Other methods which may be applicable are reviewed. Where possible, the methods described are those which require a minimum of equipment and operator skill consistent with accurate and precise analyses. Further, all the methods described have been checked by the author to determine their applicability, etc.

The problems associated with sampling, discussed previously must be borne in mind prior to any determination, and the analytical results considered in the light of these discussions.

1. Acidic Extractants

Reagents of this type are alkylphosphoric acids and aliphatic carboxylic acids.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) has been used as an extractant in commercial solvent extraction processes for many years. The solvents used contain generally 10 to 30 vol.% D2EHPA in kerosene-type diluents. A modifier is also necessary to inhibit third phase formation. Modifiers such as TBP,

isodecanol and 2-ethylhexanol are the most common.

Other alkylphosphoric acids which have been investigated as metal extractants are various mono $\{(RO)PO(OH)_2\}$ and dialkylphosphoric $\{(RO)_2PO(OH)\}$, dialkylphosphinic $\{R_2PO(OH)\}$ and alkylphosphonic $\{(RO)RPO(OH)\}$ acids, although none have been used in commercial operations.

The use of aliphatic carboxylic acids in commercial solvent extraction processes is apparently limited, at the present time, to the extraction of yttrium by Versatic 9[81], and the separation of cobalt and nickel by a $C_7 - C_9$ fraction of carboxylic acids[82]. A large amount of experimental, and some pilot plant work has been carried out using various carboxylic acids, especially for the extraction of cobalt and nickel. A review of carboxylic acids as extractants in solvent extraction processing has recently been given[39].

Titration in non-aqueous media has been employed extensively for the determination of these types of reagents in solvents. Basically, these reagents present no analytical problems in their titrimetric determination in solvents, and general methods are available in any text on non-aqueous titrations. Both indicator and potentiometric methods are adequate for end point determinations. Problems do arise when metals or extractant salts are present, and these are dealt with by the procedures given below. A titrimetric procedure is probably the fastest and most economical method of determin-

ation of acidic extractants, with adequate accuracy and precision.

Method E.1. General Procedure for the Determination of Acidic Extractants in solvents.

Reagents

Sodium methoxide solution. This can be prepared from either sodium metal or sodium methoxide. If sodium metal is used; weigh approximately 2.5 g of clean, bright, sodium metal, and cut into small pieces. Add, piece by piece, to about 500 ml of dry methanol, covering the containing vessel with a watchglass during this operation (the dissolution is best carried out in a fume hood, away from flames). When all the sodium is dissolved, dilute to one litre with methanol, and store in a tightly stoppered plastic bottle. Sodium methoxide ($NaOCH_3$) can be obtained as a white solid, which is convenient for making up solutions of this reagent. Dissolve about 5.5 g of sodium methoxide in methanol and dilute to one litre. Store in a plastic bottle. Solutions of sodium methoxide should be protected from the atmosphere as much as possible, and should be standardized frequently.

Standardization

Weigh accurately about 0.3 g of pure, dry, benzoic acid, dissolve in about 100 ml of chloroform contained in a 250-ml beaker. Add a few drops of thymol blue indicator solution and titrate with the sodium methoxide

solution to a yellow-blue end point. The equivalent weight of benzoic acid is 122.12. A blank must be determined on the same volume of chloroform as used for the standardization.

Thymol blue solution; 0.5 wt.% thymol blue in ethanol.

Chloroform.

Procedure

Transfer a suitable aliquot of the solvent to a 250-ml beaker. Add about 100 ml of chloroform, a few drops of thymol blue solution, and titrate with the standard sodium methoxide solution to a yellow-blue end point. Determine a blank on the chloroform.

$$(RO)_2PO(OH) + CH_3ONa \rightarrow (RO)_2PO(ONa) + CH_3OH \qquad [9]$$

$$R_3C\cdot COOH + CH_3ONa \rightarrow R_3C\cdot COONa + CH_3OH \qquad [10]$$

Notes

Inert diluents and modifiers do not interfere. Some solvents are quite viscous, and this must be taken into account in measuring the sample aliquot. Non-aqueous media other than chloroform can be used, such as methanol, ethanol, isopropyl alcohol, ethylene glycol, methyl ethyl ketone, and so on.

For very weak acids, basic solvents such as ethylene-diamine, dimethylformamide, pyridine, etc., may have to be used. In some cases, the end point may best be determined by potentiometric means using, for example, a

glass-calomel electrode system. For a more complete review of this topic, one of the many excellent texts on titrations in non-aqueous media should be consulted[83,84]. The method should only be used for solvents which contain no metals, alkalis or acids. For solvents containing these materials, see Method E.2.

Solvents Previously Contacted with Aqueous Solutions

For acidic extractant-containing solvents which have been contacted with acidic or basic aqueous solutions, contain metals, or have been equilibrated to form extractant salts (such as the sodium salt of D2EHPA, $\{(RO)_2PO(ONa)\}$), the sample must be treated prior to the determination of the extractant concentration. The following procedures are applicable, by which metals are stripped from the solvent, and the extractant converted to the free acid form.

Method E.2. Determination of Acidic Extractants in Solvents Containing Metals and/or Alkali Salts.

Reagents

Standard 0.1M perchloric acid solution; dissolve 8.5 ml of 70% perchloric acid in anhydrous 1,4-dioxane and dilute to one litre with dioxane.

Standardization

Weigh accurately 0.3 - 0.4 g of tris(hydroxymethyl) aminomethane, $(CH_2OH)_3CNH_2$, (equ. wt. = 121.14),

dissolve in chloroform and titrate with the perchloric acid solution using thymol blue as the indicator. Other substances suitable for standardization of the perchloric acid are potassium hydrogen phthalate, $KHC_8H_4O_4$ (equ. wt. = 204.22) and diphenylguanidine, $(C_6H_5NH)_2CNH$, (equ. wt. = 211.26). The former must be dissolved in acetic acid, and the latter may require recrystallizing from toluene if not pure. Anhydrous sodium carbonate, Na_2CO_3 (equ. wt. = 41.40), may also be used, but needs to be dissolved in acetic acid. The end points in all cases may be determined with indicators or potentiometrically. Sodium methoxide solution; (see Method E.1.). Sulphuric acid solution; 20 vol.%. Thymol blue solution; 0.5 wt.% in ethanol.

Procedure

Transfer about 30 ml of sample to a 125-ml separatory funnel. Add about 30 ml of 20 vol.% sulphuric acid and shake for 2 minutes. Allow the phases to separate and discard the lower (aqueous) phase. Repeat if necessary (see Notes). Filter the organic phase through a phase separating paper (Whatman 1PS). Transfer a suitable aliquot of the filtrate to a 250-ml beaker, add about 50 ml of chloroform and a few drops of thymol blue solution. Add sodium methoxide solution until the solution turns to a deep blue. Add perchloric acid to a blue to yellow end point. Titrate from this point to

a yellow to purple end point with the perchloric acid. This is the titration of the acidic extractant.

Notes

The following reactions are involved in the titration of a D2EHPA/H_2SO_4 mixture;

(i) Titration with $NaOCH_3$ to a blue end point -

$$(RO)_2PO(OH) + CH_3ONa \rightarrow (RO)_2PO(ONa) + CH_3OH \quad [11]$$

$$H_2SO_4 + 2CH_3ONa \rightarrow Na_2SO_4 + 2CH_3OH \quad [12]$$

(CH_3ONa in excess).

(ii) Titration with $HClO_4$ to a blue to yellow end point titrates the excess CH_3ONa -

$$CH_3ONa + HClO_4 \rightarrow CH_3OH + NaClO_4 \quad [13]$$

(iii) Titration of the sodium salt of the D2EHPA with perchloric acid to a yellow-purple end point -

$$(RO)_2PO(ONa) + HClO_4 \rightarrow (RO)_2PO(OH) + NaClO_4 \quad [14]$$

Alcohols and inert organic diluents do not interfere. It is necessary to remove metal ions from the solvent. A 20 vol.% sulphuric acid solution has been found satisfactory for many solvents, although other acids and concentrations may be necessary in some cases.

Determination of Extractant Salt Concentration

The concentration of alkali salt (sodium or ammonium) of an acidic extractant present in a solvent can be readily determined by Method E.3.

Method E.3. Determination of the Alkali Salt Concentration of an Acidic Extractant in the Solvent Phase.

Reagents

Standard perchloric acid solution; (see Method E.2.).

Thymol blue solution; 0.5 wt.% in ethanol.

Chloroform.

Procedure

Transfer a suitable aliquot of the solvent into a 250-ml beaker. Add about 100 ml of chloroform, a few drops of thymol blue solution, and titrate to a blue to yellow end point with the perchloric acid solution. Determine a blank titration on 100 ml of chloroform.

$$(RO)_2PO(ONa) + HClO_4 \rightarrow (RO)_2PO(OH) + NaClO_4 \qquad [15]$$

$$R_3C\cdot COONa + HClO_4 \rightarrow R_3C\cdot COOH + NaClO_4 \qquad [16]$$

2. Chelating Extractants

Commercially available chelating extractants are limited to the General Mills LIX reagents LIX-63*, -64, -64N, -65N and -70, and to Ashland Chemicals Kelex 100 and 120, and Media I and II. These have been produced specifically for the extraction of copper from acidic (pH 1 - 3) leach solutions. The LIX-64N is presently being used in several commercial solvent extraction plants[18 - 21]. The Kelex and Media reagents are not presently in commercial use.

*LIX-63 is not now available commercially. About 1% of this reagent is added to the other LIX reagents to improve extraction kinetics.

As received, the LIX extractants are dark brown, fairly viscous liquids, containing some 40 vol.% of the active reagent in a kerosene-type diluent. They are usually used in commercial operations as 7 - 10 vol.% solutions in a kerosene diluent.

Advantage may be taken of the weakly acidic nature of the LIX reagents ($pK_a \simeq 6.7$[76]) for their determination by titration in non-aqueous media. There are several problems associated with such an approach, however. Thus, the kinetics of the reaction of, for example, sodium methoxide with LIX reagents in a non-aqueous medium are slow. The rate can be increased by heating. Also, the dark color of the solvent solution tends to mask color changes of indicators. This problem is further complicated by the fact that the addition of alkali to solutions of LIX reagents produces a yellow color.

Perhaps one way of overcoming these problems is to add an excess of standard sodium methoxide solution to an aliquot of the LIX-kerosene solution, heat on a boiling water bath until the reaction is complete, cool and back titrate the excess alkali with standard perchloric acid in dioxane, the end point being determined potentiometrically.

A procedure generally employed in plants using LIX reagents utilises the loading capacity of the solvent for copper as a measure of the LIX concentration in the solvent[85]. Copper in the loaded solvent may be determined colorimetrically (after dilution) or by stripping the copper and determining it in the

strip liquor by a suitable method.

The Kelex reagents are substituted quinolines[76], but their actual structure has not yet been divulged. As such, they are weakly basic in nature, and are amenable to titration in non-aqueous media.

The following procedure has been found suitable for the determination of the concentration of these reagents in solvents.

Method E.4. Determination of Kelex 100 and 120 in Solvents.

Reagents

Standard perchloric acid solution; 0.1N in glacial acetic acid. Add 8.5 ml of 70% perchloric acid to about 900 ml of glacial acetic acid, and dilute to volume with glacial acetic acid. Standardise against tris(hydroxymethyl)-aminomethane (equ. wt. = 121.14), potassium hydrogen phthalate (equ. wt. = 204.22), or diphenylguanidine (equ. wt. = 41.50). Weigh a suitable quantity of the selected standard, dissolve in glacial acetic acid, and titrate with the perchloric acid solution, using either methyl violet as indicator, or potentiometrically using glass and calomel electrodes.

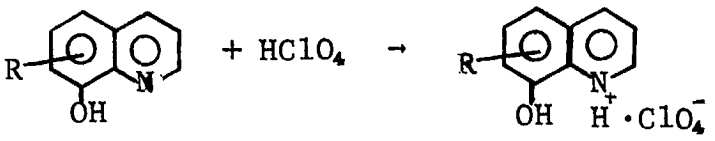
Glacial acetic acid.

Methyl violet; 0.1 wt.% in glacial acetic acid.

Acetic anhydride.

Procedure

Transfer a suitable aliquot of the solvent (Kelex 100 or 120 in a diluent) to a 250-ml beaker. Add about 100 ml of glacial acetic acid and 10 ml of acetic anhydride. Allow to stand for 10 minutes, add a few drops of methyl violet indicator, and titrate to a blue to green end point. The end point may also be determined potentiometrically using glass and calomel electrodes.



[17]

Notes

The acetic anhydride is added to remove any water present in the solvent, in order to give a sharper end point. All metals must be removed prior to the determination. This can be accomplished by stripping with a suitable acid. Up to 30 vol.% may be required to remove completely any copper or other metals which may be present. The strip solution may require warming to achieve maximum stripping efficiency. Kelex 100 and 120 are approximately 3.0 and 0.6M, respectively, as received.

3. Basic Extractants

Basic extractants are, for all industrial purposes, limited to primary, secondary, tertiary amines, and quaternary ammonium halides. Solvent extraction processes have been developed

which use primary (RNH_2), secondary (R_1R_2NH), tertiary (R_3N) and quaternary (R_4NX) amines. The ability of amines to extract metals is dependent upon the ability of a metal to form an anionic complex, such as $UO_2(SO_4)_3^=$, $CoCl_4^=$, $MoCl_4^=$, $UO_2Cl_4^=$, in aqueous solutions.

Amines which have been used in commercial operations are given in Table 2, and are long chain, high molecular weight fatty amines. Extraction of metals by these reagents occurs via an amine salt, through the reaction

$$\overline{R_3N} + H^+ + A^- \rightleftharpoons \overline{R_3NH^+A^-} \qquad [18]$$

for the case of a tertiary amine. The acid (HA) used to form this salt is usually the same as used in leaching the metal in question. The amine is equilibrated with a dilute solution of this acid (equation 19) prior to contacting with the metal-containing leach liquor.

Extraction of the metal occurs by an anion-exchange process in which the anion A^- is exchanged for an anionic metal species. In the case of the extraction of uranium, this may be illustrated as shown in equation 20.

$$2\overline{R_3N} + H_2SO_4 \rightleftharpoons \overline{\{(R_3NH^+)_2 \cdot SO_4^=\}} \qquad [19]$$

$$\overline{(R_3NH^+)_2SO_4^=} + UO_2(SO_4)_3^= \rightleftharpoons \overline{(R_3NH^+)_2UO_2(SO_4)_3} + SO_4^= \qquad [20]$$

Numerous volumetric methods, in non-aqueous media, have been proposed for the determination of both micro and macro quantities of amines. The non-aqueous media used include acetic acid[86], methyl ethyl ketone[87], pyridine[88], nitromethane[89], methyl cellosolve[90], dioxane[91], benzene[92], and some mixtures of

these. End point determination is usually by indicator or potentiometrically. Non-aqueous titrations are also very useful for the individual determination of primary, secondary and tertiary amines in mixtures of these reagents.

Amines used in solvent extraction processing usually have pK_B values in the range 2 - 6, that is, they are not particularly weak bases. Consequently, they can be readily determined in a non-aqueous medium such as chloroform. Most methods appear to use glacial acetic acid, in which the basicity of the amines is increased. Acetic acid has one advantage over hydrocarbons for the determination of total amine in amine mixtures which contain significant amounts of primary, secondary or tertiary amines. Thus, glacial acetic acid tends to cancel out any basicity difference between the various amine components.

For the titration of amines in non-aqueous media they must be present in the organic phase as the "free amine". Since samples of amine-containing solvents from solvent extraction processes rarely contain the amine in the free form, treatment prior to analysis is necessary. Further, metals present in the solvent have to be removed. Procedures for sample preparation are as follows.

Sample Preparation for Amine-Containing Solvents

Procedure P.1.

Place 3 - 4 times the volume of sample required for analysis into a separatory funnel. Add about twice

the volume of a 10 wt.% solution of sodium carbonate and shake for one minute. Allow the phases to separate and discard the aqueous phase. Repeat this extraction twice more. Shake the organic phase three times with an equal volume of water, discarding the aqueous phase each time. Do not shake too hard or emulsions may form. Filter the organic phase through a Whatman 1PS phase separating paper to remove entrained water. Analyse the filtrate by one of the methods for the determination of amine given below.

Notes: Some metals, for example uranium, can also be stripped from the organic phase by sodium carbonate solution. If metals are present which are not stripped by sodium carbonate, they require stripping by acid (next procedure).

Procedure P.2.

Place 3 - 4 times the volume of sample required for analysis into a separatory funnel. Add an equal volume of 20 vol.% sulphuric acid and shake for one minute. Allow the phases to separate, and discard the aqueous phase. Repeat if necessary to remove all metals. The sulphuric acid present in the organic phase, as amine sulphate, can be removed either by contacting the organic phase with a sodium carbonate solution (Procedure 1 above), or by using solid calcium hydroxide (see Method E.8).

Method E.5. Determination of Total Amine in a Solvent.

Reagents

Standard perchloric acid solution; 0.1N. See Method E.4.

Glacial acetic acid.

Gentian violet, crystal violet or methyl violet indicator; 0.1 wt.% in glacial acetic acid.

Procedure

Transfer a suitable aliquot of the sample to a 250-ml beaker, add about 100 ml of glacial acetic acid and a few drops of indicator solution. Titrate with the perchloric acid solution to a blue to green end point. The end point may also be determined potentiometrically, using glass and calomel electrodes.

$$R_3N + HClO_4 \rightarrow R_3NH^+ \cdot ClO_4^- \qquad [21]$$

Method E.6. Determination of Total Amine in a Solvent.

Reagents

Standard perchloric acid solution; 0.1N. See Method E.2.

Chloroform.

Thymol blue indicator; 0.1 wt.% in ethanol.

Procedure

Transfer a suitable aliquot of the sample to a 250-ml beaker. Add about 100 ml of chloroform, a few drops of indicator solution, and titrate with the perchloric acid solution to a blue to yellow end point.

Notes

Both methods are suitable for the determination of total amine, irrespective of whether the major component is primary, secondary or tertiary amine. For amines containing >2% of another amine, Method E.5. is to be prefered.

Method E.7. Determination of Tertiary Amine in the Presence of Primary and Secondary Amines.

Reagents

Standard perchloric acid solution; 0.1N. See Method E.4.

Glacial acetic acid.

Acetic anhydride.

Procedure

Transfer a suitable aliquot of sample to a 150-ml beaker. Add 25 ml of glacial acetic acid and 25 ml of acetic anhydride. Allow to stand for 30 minutes. Titrate with the perchloric acid solution using indicator or potentiometric end point detection (Method E.4.).

Notes

Acetic anhydride acetylates primary and secondary amines; tertiary amines are not acetylated and are determined by titration with perchloric acid.

The concentration of primary plus secondary amine in

tertiary amine can be obtained by determination of the total amine by Method E.5., and the tertiary amine by Method E.7., the difference being due to primary plus secondary amine. Most commercial tertiary amines contain only a small amount of primary amine (<1%), and this will probably be lost from the solvent during continuous solvent extraction operations as a water soluble salt.

Method E.8. Determination of Amine in Solvents Used in Uranium Extraction.

Reagents

Standard perchloric acid solution; 0.1N in dioxane (see Method E.2.).

Chloroform.

Calcium hydroxide.

Thymol blue solution; 0.1 wt.% in ethanol.

Procedure

Place about 25 ml of the amine-containing solvent in a 125-ml Erlenmeyer flask. Add about 5 g of calcium hydroxide, stopper and shake for 1 minute. Filter through a Whatman No. 1PS phase separating paper. Transfer an aliquot of the filtrate to a dry 125-ml Erlenmeyer flask, add about 20 ml of chloroform and a few drops of thymol blue solution. Titrate with the standard perchloric acid solution to a yellow to violet end point.

Notes

This method has been used for many years in uranium solvent extraction plants and R and D laboratories. Alcohols such as isodecanol and 2-ethylhexanol, added to the solvent as third phase and emulsion inhibitors (usually 2 - 5 vol.%) do not interfere.

Both uranium and sulphuric acid are removed by the calcium hydroxide.

Method E.9. Determination of Quaternary Ammonium Salts.

Reagents

Standard perchloric acid solution; 0.1N in glacial acetic acid (see Method E.4.).

Glacial acetic acid.

Mercuric acetate solution; 5 wt.% in glacial acetic acid.

Crystal violet solution; 0.1 wt.% in glacial acetic acid.

Procedure

Transfer a suitable aliquot of sample to a 250-ml beaker. Add about 100 ml of glacial acetic acid, 10 ml of mercuric acetate solution and stir for about 10 minutes. Add a few drops of crystal violet solution and titrate with the perchloric acid solution to a colorless end point. The end point can also be determined potentiometrically using glass

and calomel electrodes.

$$2R_4N^+\cdot X^- + Hg(CH_3COO)_2 \rightarrow 2R_4N^+\cdot CH_3COO^- + HgX_2 \quad [22]$$

$$R_4N^+\cdot CH_3COO^- + HClO_4 \rightarrow R_4N^+\cdot ClO_4^- + CH_3COOH \quad [23]$$

Notes

Metals must be stripped from the solvent before determination of the quaternary ammonium salt.

Solvents Containing Mixed Extractants

Mixtures of various extractants have been shown to exhibit both synergistic and antagonistic effects in the extraction of metals[93]. In investigations of this type, it is useful to determine the composition of the solvents with respect to extractants, especially in pilot plant operations, or after the solvent has been used in many extraction-strip cycles.

There appears to be only one reported method for the determination of mixed extractants in a solvent, namely the determination of amine and alkylphosphate in kerosene solution containing TBP[94].

Method E.10. Determination of Amine and Alkylphosphoric Acid in a Mixed Solvent.

Reagents

Sodium-methoxide solution; (see Method E.1.).

Perchloric acid solution; 0.1N in dioxane (see Method E.2.).

Calcium acetate.

Chloroform.

Thymol blue solution; 0.1 wt.% in ethanol.

Procedure

Transfer about 50 ml of solvent to a 125-ml separatory funnel and add about 25 ml of 20 vol.% sulphuric acid. Shake for 1 - 2 minutes, allow the phases to separate, and discard the lower aqueous phase. Repeat if necessary (see Notes below). Filter the organic phase through a Whatman phase-separating paper. Take a suitable aliquot of the filtrate and transfer to a 250-ml beaker. Add about 100 ml of chloroform and a few drops of thymol blue solution. Add sodium methoxide solution to a deep blue colored solution. Add perchloric acid solution to a blue to yellow end point. Titrate from this point with perchloric acid solution to a yellow to purple end point. This titrates both the alkylphosphoric acid and amine.
To another portion of the filtrate add 5 g of calcium acetate and mix for 1 min. Filter off the solids and transfer a suitable aliquot of the filtrate to a 250-ml beaker. Add about 100 ml of chloroform, a few drops of thymol blue solution, and titrate with perchloric acid solution to a yellow to purple end point. This titrates the amine only. Determine blank values on the same volume of chloroform used in the titrations.
Addition of sodium methoxide:

$$(R_3N)_2 \cdot H_2SO_4 + 2CH_3ONa \rightarrow 2R_3N + 2CH_3OH + Na_2SO_4 \downarrow \qquad [24]$$

$$(RO)_2PO(OH) + 2CH_3ONa \rightarrow (RO)_2PO(ONa) + 2CH_3OH \quad [25]$$

$$H_2SO_4 + 2CH_3ONa \rightarrow 2CH_3OH + Na_2SO_4\downarrow \quad [26]$$

Addition of perchloric acid:

$$CH_3ONa(XS) + HClO_4 \rightarrow CH_3OH + NaClO_4 \quad [27]$$

Titration with perchloric acid (amine plus alkylphosphoric acid):

$$R_3N + HClO_4 \rightarrow R_3NH^+\cdot ClO_4^- \quad [28]$$

$$(RO)_2PO(ONa) + HClO_4 \rightarrow (RO)_2PO(OH) + NaClO_4 \quad [29]$$

Addition of calcium acetate:

$$(R_3N)_2\cdot H_2SO_4 + (CH_3COO)_2Ca \rightarrow CaSO_4 + 2R_3NH^+\cdot CH_3COOH \quad [30]$$

Titration with perchloric acid (amine):

$$R_3NH^+\cdot CH_3COO^- + HClO_4 \rightarrow R_3NH^+\cdot ClO_4^- + CH_3COOH \quad [31]$$

Notes

The method has been used for the determination of a tertiary amine and D2EHPA or monoheptadecyl phosphoric acid in kerosene solutions containing TBP[94].

4. Neutral Extractants

For all commercial solvent extraction operations only one neutral (or solvating) extractant, TBP, is used which is diluted in kerosene. Methyl isobutyl ketone is used undiluted, and hence does not require analysis in the solvent phase.

Tributyl phosphate has seen considerable use in the nuclear industry, where it is used for the extraction and separation of radioactive species[26]. It has also been used successfully commercially for the separation of zirconium and

hafnium[95]. Other applications include the extraction of uranium from impurities prior to the production of high grade UO_2 and UO_3[29].

This extractant has seen little use commercially in the extraction of base metals, although a number of papers have been published regarding its use in this area[96-99]. TBP is also used as a modifier, especially in solvents containing D2EHPA[13]. For this purpose, about 5 vol.% is added to the solvent.

Methods for the determination of TBP in kerosene-type diluents are of varied nature. Volumetric[100], and colorimetric[101], flame photometric[102], gas chromatographic[103-105] and paper chromatographic[106] methods have been described.

One volumetric method is based on the fact that TBP forms an adduct, $TBP \cdot HNO_3$, under certain conditions when contacted with nitric acid. The nitric acid extracted is titrated and calculated as TBP[107]. An analogous method uses the formation of a TBP-uranium complex, $UO_2(NO_3)_2 \cdot 2TBP$, the uranium being determined by titration with EDTA using xylenol orange as the indicator[108]. A similar method is used for micro amounts of TBP, the uranium being determined colorimetrically with Arsenazo I[108]. These methods are also suitable for the determination of butyl dibutylphosphonate, tributylphosphine oxide and trioctylphosphine oxide. Other colorimetric methods, again employing the extraction of uranium but measuring the

yellow TBP-uranium complex color, in both the visible and UV ranges, have been described[109]. Infrared spectroscopy has also been employed for the determination of TBP in kerosene-type diluents[110]. Other reported methods involve turbidimetry[111], dielectric properties[112], specific gravity[113], decomposition and determination of phosphorus[114].

The following methods have been found satisfactory by the author for the determination of TBP in kerosene-type diluents.

Method E.11. Volumetric Determination of Tri-n-butyl Phosphate.

Reagents

Standard sodium hydroxide solution; 0.1 or 0.2M. Standardize against potassium hydrogen phthalate, $KHC_8H_4O_4$, (equ. wt. = 204.22).

Bromothymol blue solution; 0.1 wt.% in ethanol.

Procedure

Transfer a suitable aliquot of sample to a separatory funnel. Add an equal volume of 8M nitric acid solution and shake for 2 minutes. Allow the phases to separate and discard the aqueous phase. Repeat this procedure twice more. Filter the organic phase through a Whatman 1PS phase separating paper into a 250-ml beaker. Wash the paper with kerosene, add 100 ml of water to the beaker, a few drops of indicator solution, and titrate with the standard sodium hydroxide solution. Mix thoroughly during the titration.

Notes

Metals must be stripped from the organic phase prior to the determination of TBP. If they are not stripped by nitric acid (eg., zirconium), use a 10 vol.% solution of sodium carbonate. A volume increase occurs on contacting the TBP-kerosene solution with nitric acid, thus the whole sample aliquot contacted with nitric acid should be used. If only a portion is taken (after forming the $TBP \cdot HNO_3$ adduct), the following volume increase must be considered in the calculations: the volume of one mole of nitric acid in a solution of TBP, of any concentration, is taken as 41.5 ml[115]. If necessary the TBP-kerosene solvent can be diluted, prior to the TBP determination, with kerosene of similar solution.

Method E. 12. Spectrophotometric Determination of Tri-n-butyl Phosphate.

Reagents

Uranyl nitrate solution; saturated aqueous solution.

Aluminum nitrate solution; saturated solution.

Procedure

Place 25.0 ml of sample into a separatory funnel. Add 3 ml of each of the uranyl nitrate and aluminum nitrate solutions, and shake for 5 minutes. Allow the phases to separate and discard the aqueous phase. Filter the

organic phase through a Whatman 1PS phase separating paper. Measure the absorbance at 415 nm for TBP concentrations of about 1 - 7 vol.%, and at 280 nm for concentrations of 0.02 - 1 vol.%, against a diluent blank carried through the procedure.

Notes

Metals present in the sample must be removed prior to the determination.

Method E.13. Gas Chromatographic Determination of Tri-n-butyl Phosphate.

Apparatus and Conditions

Gas chromatograph.

Column; 6 ft x 1/4 inch, stainless steel, packed with 3% OV-1 on Chromosorb W, 60/80 mesh.

Oven temp.; 175°C.

Injection port temp.; 200°C.

Carrier gas; helium.

Gas flow rate; 70 ml/min.

Detector; thermistor.

Syringe; 10 µl.

Recorder; 1 mA full-scale deflection.

Procedure

Calibration - Prepare solutions of TBP, in the diluent used in the solvent extraction process, containing 1, 2, 3, 5, 7 and 10 vol.%, or any convenient range to

cover the expected concentrations in samples to be analysed. Inject a suitable sample (1 - 5 µl) into the chromatograph. Calibration can be on the basis of peak height or peak area. The latter gives a straighter line calibration curve. Plot against vol.% of TBP.

Analysis of samples - If the sample contains metals or acids, contact with sodium carbonate solution prior to analysis (Procedure P.1.). Inject a suitable aliquot of the sample into the chromatograph. Determine the TBP concentration from the calibration graph.

Notes

The conditions given above were found suitable for use with a F and M 700 gas chromatograph, but may be varied to suit other chromatographs or conditions. A standard TBP solution should be run frequently with samples. The method is very sensitive, and <1 µg of TBP can be detected. A standard deviation of about ±0.25% over the range 1 - 5 vol.% TBP is to be expected. A typical chromatogram of TBP in kerosene (Shell 140 Flash Naphtha) is shown in Fig. 4, together with a typical calibration curve. Dibutyl phosphate, a degradation product of TBP which occurs in some processes, does not interfere. Non-polar substrates other

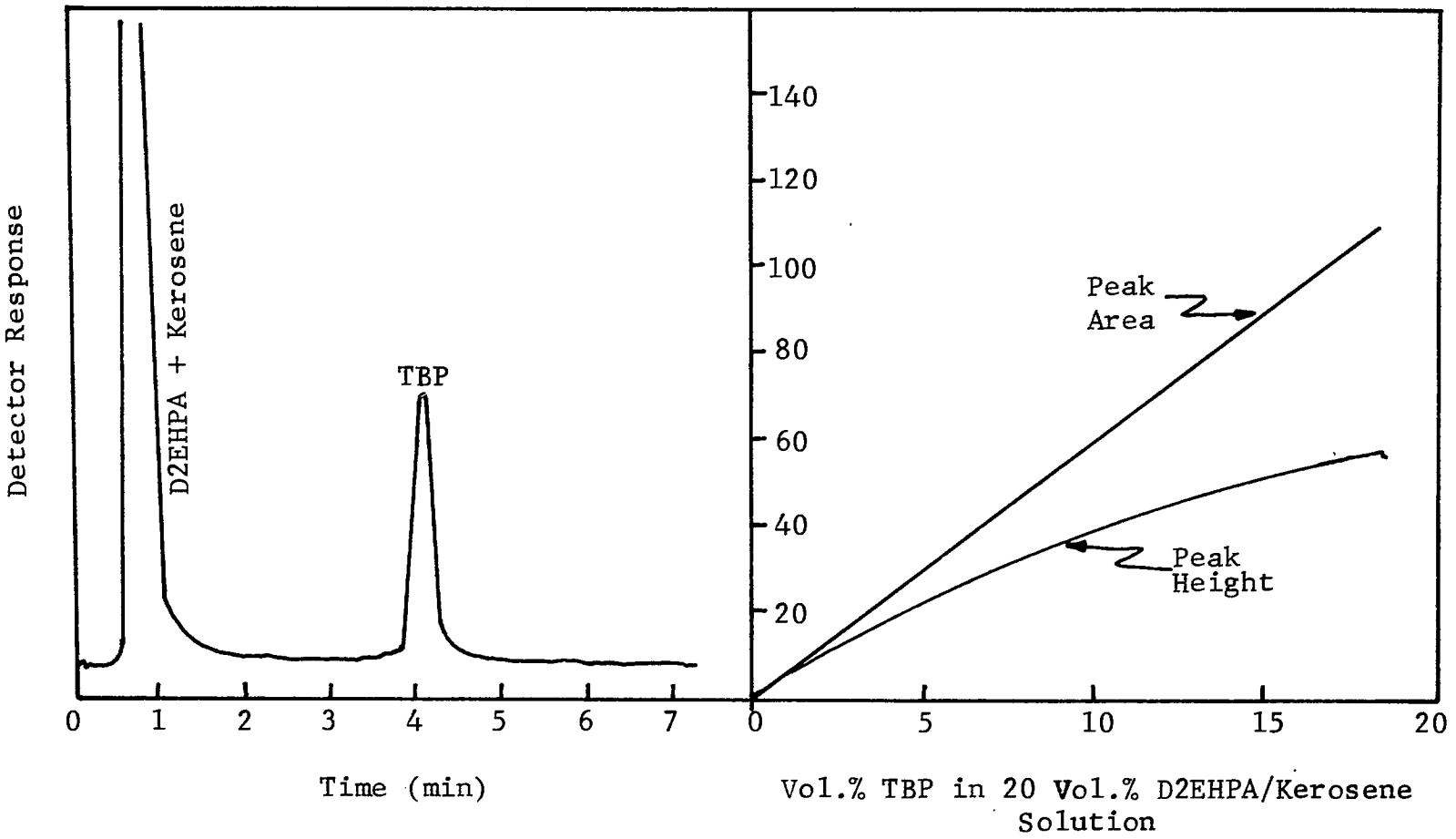


Fig. 4: Typical Chromatogram and Calibration Curve for TBP in D2EHPA/Kerosene Solution

than OV-1, such as Apiezon L, N, silicone oil and silicone grease, may be used.

MODIFIERS

The formation of a third phase (two organic phases) and emulsions present considerable problems in solvent extraction processing. To reduce or inhibit these effects, modifiers are added to the solvent, or the diluent is changed[118]. In commercial operations, modifiers are limited to aliphatic alcohols and TBP (Table 4). These reagents are soluble in the aqueous phase to some extent, and consequently are lost from the solvent. Consequently, analysis of the solvent not only entails determination of extractant, but also of the modifier.

There appear to be no simple methods for the analysis of alcohols in solvent mixtures reported in the literature. Most methods for the determination of alcohols in organic solution are time consuming and may require close control[116]. Determination of alcohols, such as isodecanol and 2-ethylhexanol, in kerosene-extractant mixtures by gas chromatography, appears to be impracticable. This is due to components of the kerosene masking the alcohol peaks[117]. However, little work has been done or reported on this approach.

One approach to the problem of the determination of alcohols in solvents which appears very promising is the use of the red-brown complex formed between vanadium (V), 8-hydroxyquino-

line and an aliphatic alcohol[186-190]. A similar complex (yellow) which has been used is that formed with acetylacetone in place of 8-hydroxyquinoline[189]. This latter approach is not as sensitive as the former, and would probably be more suitable at the 2 - 5 vol.% level of alcohol in the solvent. Metals present in the solvent would have to be removed by stripping, since the acetylacetone, and especially the 8-hydroxyquinoline, form colored complexes with some metals.

The determination of TBP, when used as a modifier in solvents containing D2EHPA, can be determined by gas chromatography, as described in Method E.13. The D2EHPA has approximately the same retention time as kerosene, and does not interfere.

ANALYSIS OF RAFFINATES

The composition of raffinates from solvent extraction processes will vary within a process, and from process to process. In a single process the extraction and scrub raffinates may be expected to have fairly constant compositions, especially if the feed and scrub solution compositions are constant. Variations should then only occur as a result of upsets, such as pump failure, solution surges, or during start-up after a shut-down period.

Raffinates from similar processes may vary significantly in composition as a result of different feed and scrub solutions. Because of such variations in raffinate compositions the methods of analysis given below may not be directly applicable to all

raffinates from similar processes. For example, some unit processes used for feed preparation to a solvent extraction circuit such as leaching, filtration, thickening and precipitation, may use reagents which interfere with the determination of solvent extraction reagents in raffinate samples. It is advisable to determine beforehand whether such is the case. In fact, each method of analysis should be investigated thoroughly with regard to its applicability to the analysis of any sample. Attention must also be paid to sampling techniques in both the plant and in the laboratory. This point cannot be emphasized too strongly.

Few methods are available for the determination of solvent components in raffinates. Many methods have been reported for the determination of organic compounds such as acids, bases and alcohols, in water. In most cases, these methods are not applicable to raffinate solutions, for obvious reasons. Further, raffinates will contain all the components of a solvent (extractant, diluent and modifier), which will not necessarily be in the ratio in which they are present in the solvent.

DETERMINATION OF EXTRACTANTS IN RAFFINATES

1. Acidic Extractants

There are a number of methods reported in the literature for the determination of organic acids in aqueous solutions. Some carboxylic acids can be separated from the inorganic constituents of a solution by steam distillation. Shaova et al.[119] employed this approach, and determined monocarboxylic acids in the distillate

by polarography. Gas chromatography has been used for the determination of carboxylic acids in aqueous solutions[120,121]. Low molecular weight acids have been separated on ion-exchange resins and determined in the eluates by gas chromatography[122]. Others have used gas chromatography with varying degrees of success[123-125]. Baker[126] has reported the determination of volatile fatty acids in water at the 10 ppm level by gas chromatography. One major problem with gas chromatography for the determination of total acids such as Versatic and Naphthenic acids in aqueous solution is that these are not pure compounds, but mixtures of several similar acids. The concentration of the components also varies, to some degree, from batch to batch, or run to run. For example, Versatic 911, as received, contains at least five components, and these have been shown to vary significantly between two different samples[117]. Another point to remember is that the various components of the acid extractant may have different solubilities in the aqueous phase, which could present problems in interpreting the analyses in terms of extractant loss.

Colorimetric methods of analysis for acids include the use of rhodamine and butylrhodamine for aromatic carboxylic acids, in an extraction-photometric procedure[127].

Methods which are probably the most appropriate for the determination of fatty acids in solvent extraction raffinates are those based on the formation of a metal-carboxylic acid complex. This approach is similar to that employed for the determination of

D2EHPA and the LIX reagents. Such methods have been described[128-134], and could almost certainly be modified to determine carboxylic acid extractants, such as those given in Table 2, in raffinates.

Except for that given below, there appear to be no methods in the literature for the quantitative determination of trace amounts of alkylphosphoric acids in solvent extraction raffinates. Alkylphosphates in aqueous solution have been determined indirectly by oxidation to phosphoric acid, followed by determination of the phosphorus by conventional methods. This approach assumes that all the phosphorus determined results from the organophosphate. The presence of TBP in the solvent, or phosphorus in the feed solution, nullifies this approach.

Phosphine oxides in aqueous solution have been determined by O'Laughlin, Sealock and Banks[135]. The method is based on the formation, in acid solution, of a yellow adduct between the phosphine oxide, titanium(IV) and thiocyanate, which is extracted into chloroform or carbon tetrachloride.

The method given below for the determination of D2EHPA[136] is based on the formation of a brown complex formed between iron(III) thiocyanate and D2EHPA, which is extracted into carbon tetrachloride and determined photometrically.

Method R.1. Determination of D2EHPA in Raffinates.

Reagents

Ferric thiocyanate solution; approx. 0.4M. Dissolve 15 g of ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$ and 6 g of ammonium thiocyanate in about 80 ml of water. Adjust to pH 2.9

with a saturated aqueous solution of ammonium acetate and dilute to 100 ml. Prepare fresh daily.

Carbon tetrachloride.

Toluene.

Procedures

(i) Solutions: Adjust an aliquot (containing not more than 0.1 g Cu) of up to 25 ml of sample solution to about pH 2.9 by the addition of dilute sulphuric acid or saturated ammonium acetate solution and transfer quantitatively to a 125-ml separatory funnel. Alternatively, the sample aliquot may be transferred to the separatory funnel and the pH adjusted in the funnel with the aid of a combination electrode. Add 25 ml of the ferric thiocyanate solution and mix thoroughly. Add 15.0 ml of carbon tetrachloride, stopper the funnel and shake vigorously for 2 minutes. Allow the phases to separate and filter the lower (organic) phase through a Whatman No. 1PS phase separating paper. Measure the absorbance at 430 nm in a 5-cm cell, with the spectrophotometer zeroed on a blank carried through the procedure on 20 ml of water. Determine the amount of D2EHPA from a calibration curve, obtained with known amounts of D2EHPA as described above.

(ii) Slurries - Total D2EHPA: Weigh a suitable sample and the container. Adjust the pH to about 2.9 and transfer quantitatively to a 125-ml separatory funnel with a

minimum amount of methanol. Dry the container and weigh to determine the weight of sample. Add 25 ml of the ferric thiocyanate solution, mix, and add 15 ml of toluene and shake for two minutes. Allow the phases to separate, discard the solids and aqueous phase and filter the organic phase through a Whatman No. 1PS phase separating paper. Measure the absorbance at 430 nm in a 5-cm cell against a blank carried through the procedure, but without the addition of ferric thiocyanate solution. Determine the amount of D2EHPA from a calibration curve obtained on known amounts of D2EHPA, as described under solutions.

(iii) Slurries - Determination of D2EHPA in the aqueous and solid phases: Centrifuge the sample, which should be taken from the plant in a suitably sized centrifuge tube, and decant the aqueous phase. If the aqueous phase is less than about 25 ml, decant into a 125-ml separatory funnel, adjust the pH to 2.9, and determine the D2EHPA as described under solutions. Alternatively, the aqueous decant may be transferred to a suitable volumetric flask, diluted to volume and an aliquot taken for analysis. Repulp the solids four times with sufficient methanol to provide about 50% solids. Centrifuge after each repulp and combine the methanol decants. Dilute to volume with methanol and take a suitable aliquot

for analysis as described under solutions. Dry the solids at 110°C and calculate the per cent solids in the slurry.

Notes

No interference in the determination was found from up to 0.5 g of each of the following ions: Fe(III), Co(II), Ni(II), Zn(II), Mn(II), Ca(II), Mg(II), V(V), SO_4^{2-}, Cl^- and NO_3^-. Copper(II) interferes if more than 0.1 g is present in the sample aliquot, giving low results. An amount of 0.5 g of metal ion in a 25 ml aliquot is equivalent to 20 g metal/l, and for the maximum amount of copper tolerated, 4 g/l. In the determination of total D2EHPA in slurries, the removal of the solids from the separatory funnel is greatly facilitated if a funnel with a teflon tap, in which the hole has been enlarged, is used.

2. Chelating Extractants

Methods for the determination of the General Mills Liquid Ion-Exchange Reagents LIX-63, LIX-64 and LIX-64N in aqueous raffinates have only recently appeared in the literature[137]. Methods for the other commercially available chelating extractants, LIX-70, Ashland Chemical Kelex 100 and 120, and Media I and II, have not been published.

The procedures given below are based on the ability of all these chelating reagents to extract copper from acid solutions.

The copper chelate is extracted into carbon tetrachloride, and determined photometrically. They are suitable for the determination of these reagents in the ppm range in aqueous raffinate solutions.

Method R.2. Determination of LIX-63, LIX-64, and LIX-64N in Aqueous Raffinates.

Reagents

Copper nitrate solution. Stock solution; prepare a 25 wt.% solution of copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, in water. Reagent solution; adjust the stock solution to pH 3.75 by the addition of a saturated aqueous solution of ammonium acetate. Prepare the copper reagent solution just before use.

Carbon tetrachloride and toluene.

Procedures

(i) Solutions: Measure an aliquot of up to 25 ml of the sample into a beaker and adjust the pH to 3.8 with either dilute sulphuric acid or saturated ammonium sulphate solution. Transfer to a 125-ml separatory funnel and rinse the beaker into the funnel with a minimum amount of methanol. Add 25 ml of the copper reagent solution and 10.0 ml of carbon tetrachloride. Shake vigorously for 2 minutes and allow the phases to separate. Filter the organic phase through a Whatman No. 1PS phase separating paper and measure the absorbance at the appropriate wavelength

against a carbon tetrachloride blank. The optimal wavelengths are:

LIX-63 : 425 nm
LIX-64 : 365 nm
LIX-64N: 380 nm

(ii) Slurries - Determination of total LIX reagent: Weigh a suitable sample and container. Adjust the pH to about 3.8 and transfer to a 125-ml separatory funnel with a minimum amount of methanol. Weigh the dried container to determine the weight of sample. Add 25 ml of copper reagent solution, 10.0 ml of toluene and shake for 2 minutes. Allow the phases to separate, discard the solid and aqueous phases, and filter the organic phase through a Whatman No. 1PS phase separating paper. Measure the absorbance in a 1-cm cell, at the appropriate wavelength, against a sample blank carried through the procedure but without the addition of the copper solution.

(iii) Slurries - Determination of LIX reagents in the aqueous and solid phases: Centrifuge the sample, which should be taken from the plant in a suitably sized centrifuge tube, and decant the aqueous phase. If the aqueous phase is less than about 25 ml, decant into a 125-ml separatory funnel, adjust the pH to 3.8, and determine the LIX reagent as described under solutions. Alternatively, the aqueous decant may be transferred to

a suitable volumetric flask, diluted to volume and an aliquot taken for analysis. Repulp the solids four times with sufficient methanol to give about 50% solids. Centrifuge after each repulp and combine the methanol decants. Dilute to volume with methanol and take a suitable aliquot for analysis as described under solutions. Dry the solids at 110°C and determine the per cent solids in the slurry.

Notes

No interference in the determination of LIX-63, -64, and -64N is given in the presence of up to 0.5 g of each of the following ions: Fe(III), Cu(II), Ni(II), Zn(II), Mn(II), Cr(III), V(V), SO_4^{2-} and Cl^-. If the anion concentration is high, pH adjustment may cause some precipitation, but this does not appear to affect the determination. In the determination of total LIX reagent in slurries the removal of the solids from the separatory funnel is greatly facilitated if a funnel with a teflon tap, in which the hole has been enlarged, is used. A relative standard deviation of about ± 2% is given in the determination of LIX reagents in both the aqueous and solid phases. This procedure should be directly applicable to the determination of LIX-70 in aqueous raffinates.

The method given below for the determination of Kelex 100 and 120 in aqueous raffinates was developed by the Ashland Chemical Company[138]. It is rather a long procedure, and could probably be shortened considerably by using separatory funnels for contacting the sample, reagents and kerosene. There seems to be no reason why a procedure similar to that given above for the LIX reagents should not be applicable.

There appear to be no analytical methods available for the determination of Ashland Chemicals reagents Media I and Media II in aqueous raffinates. Here again, application of the principles used in the methods for D2EHPA and the LIX reagents should prove useful.

Method R.3. Determination of Kelex 100 and 120 in Aqueous Raffinates.

Reagents

Copper sulphate; $CuSO_4 \cdot 5H_2O$.

Sulphuric acid; 0.5N.

Kerosene (Napoleum 470).

Methanol.

Procedure

Transfer a suitable aliquot of the raffinate sample to a beaker, and adjust the pH to 3 - 4 using 0.5N sulphuric acid (pH meter). Add copper sulphate to provide a 4 wt.% solution, and mix, using a magnetic stirrer, until the solid has dissolved. Add, by pipette, 10.0 ml of kerosene,

and stir vigorously for two hours. Pour the two phases into a separatory funnel and allow to separate. Discard the aqueous phase, and either filter the organic phase through a Whatman 1PS phase separating paper, or centrifuge. Measure the absorbance at 438 nm against a water blank carried through the procedure. Determine the concentration of Kelex reagent by reference to a calibration graph constructed by carrying known amounts of Kelex (in methanol solution) through the procedurs.

Notes

The kinetics of extraction of copper by Kelex reagents are faster than for the LIX reagents. Consequently, it would appear that the extraction time of 2 hours given in the above procedure is not necessary if an approach similar to that used for the determination of LIX reagents in raffinates is used (Method R.2.).

3. Basic Extractants

The determination of micro and macro amounts of amines in aqueous solutions has been investigated quite thoroughly, and a number of methods have been reported in the literature. Most employ the formation of a colored complex of the amine, and a photometric finish.

Critchfield and Johnson[139] determined primary amines in the presence of secondary and tertiary amines by reacting the primary amine with an aqueous reagent containing cupric chloride,

salicylaldehyde and triethanolamine. The complex formed was extracted into hexanol, and the copper in the hexanol determined photometrically with bis (2-hydroxyethyl) dithio carbamic acid. The yellow-green color formed between amines and alcoholic cupric chloride in aqueous solution, and extracted into chloroform, was used by Hershensen and Hume to determine total amine in aqueous solution[140].

Silverstein[141] used methyl orange, at pH 3 - 4, to form an extractable colored adduct for the determination of total amines. In the presence of salicylaldehyde, primary amines did not react. In the presence of acetic anhydride, only tertiary amines are determined. The procedure was modified by Larrik[142] for use in the field. Irving[143] employed bromocresol green for the determination of amines in $0 - 10^{-6}$ molar solutions. The adduct was extracted into dichloroethane and determined colorimetrically. Trifluoroacetic anhydride was used by McCurdy and Reiser[144] to form trifluoracetyl derivatives of amines in aqueous solution, followed by extraction into n-hexane and determination by gas chromatography. Formation of N-substituted cinnamides of primary and secondary amines was the basis of a colorimetric method for the determination of these amines by Hong and Connors[145].

The ability of small amounts of primary amines to reduce the absorption of a copper-EDTA solution at 720 nm was used by Citron and Mills[146] to determine primary amines. Succinaldehyde has also been used for the spectrophotometric determination of primary amines[147,148].

Dyes have proved to be popular chromophoric reagents for amines. These include bromocresol purple[149,150], bromothymol blue[151], bromocresol green[150], and phenol red[150], and methyl orange[152]. Other reagents include picric acid[153], ninhydrin[154], 3, 5-dinitrobenzoyl chloride[155], 3-chloro-3(10,12-dioxodi-indeno-[1,2-b; 2', 1'-e] phthalide[156], aconitic anhydride[157], and chloranil[157].

The formation of an extractable complex, formed in aqueous solution between amines and cobalt thiocyanate has been used for the determination of symmetrical fatty amines in raffinates from uranium solvent extraction plants[158]. This method has been modified to determine non-symmetrical amines[159]. Further modifications involve the use of ferric thiocyanate in place of the cobalt thiocyanate[160], and the extraction of amine into carbon tetrachloride prior to the formation of the amine-cobalt thiocyanate complex[161]. Small amounts of long chain amines in aqueous solutions have also been determined using Erdmann's salt[162].

Volumetric methods for the determination of amines in aqueous solutions have included the use of eosin[77] and sodium lauryl sulphate[163]. Amine salts in aqueous solution have been converted to free amines in a "fore column" packed with an acid coated support in a gas chromatograph. The amines were then determined by gas chromatography on an analytical column attached to the end of the "fore column"[164].

Of the methods available, the one given below[165] has been found to be applicable to most amine extractants, and is simple and accurate. All of the common amines, primary, secondary, tertiary and quaternary, can be determined at the ppm level in aqueous raffinates.

Method R.4. Spectrophotometric Determination of Primary, Secondary, Tertiary and Quaternary Amines in Aqueous Raffinates.

Reagents

Bromophenol blue solution; dissolve 50 mg of the dye in ethanol and dilute to 100 ml with ethanol. Prepare fresh each day.

Sulphuric acid; 0.5N.

Methanol.

Chloroform.

Procedures

(i) Aqueous Solutions: Transfer into a 60-ml separatory funnel up to 10 ml of sample. Add 15 ml of water and adjust the pH to between 1 and 3. Add 1.0 ml of bromophenol blue solution, 10.0 ml of chloroform, and shake for 2 minutes. Allow the phases to separate and run the organic phase into dry 15-ml centrifuge tubes. Stopper and centrifuge for 2 minutes. Measure the absorbance in 1-cm cells at 410 nm, against a blank carried through the solution on water. The absorbance

should be determined within 30 minutes. Calibration: Prepare a standard solution containing 100 µg of amine per ml, in methanol. Transfer aliquots containing up to 100 µg of amine to 60-ml separatory funnels, add 15 ml of water, adjust the pH to 1 to 3, and continue as described above.

(ii) Slurries - Determination of Amine in the Aqueous and Solid Phases: Centrifuge the sample, which should be taken from the plant in a suitably sized centrifuge tube, and decant the aqueous phase into a container. Take a suitable aliquot and determine the amine as described above under aqueous solutions. Repulp the solids four times with sufficient methanol to give about 50% solids. Centrifuge after each repulp and combine the methanol decants. Dilute to volume with methanol and take up to 3 ml of this solution for analysis as described under aqueous solutions. Dry the solids at 110°C and calculate the per cent solids in the slurry sample.

Notes

If more than 3 ml of the methanol solution are taken for analysis, the same volume of methanol must be added to the blank solution. Volumes of methanol greater than 3 ml give high blanks as a result of increased solubility of the dye in the chloroform-methanol mixture.

A convenient size for the sample centrifuge tube is 250 ml, and from 100 to 200 ml of sample (slurry) has been found to be suitable.

4. Neutral Extractants

The solubility of TBP in aqueous solutions has been determined using ^{32}P[166]. O'Laughlin et al.[135] have reported a spectrophotometric procedure for the determination of phosphine oxides in aqueous solutions, based on the formation of an extractable adduct formed between the oxide, titanium(IV) and thiocyanate. Cationic interference was not investigated. A similar approach, in which a metal complex formed in the aqueous phase is extracted into an inert hydrocarbon, has been investigated for the determination of TBP[117]. Ferric thiocyanate, for example, can be used, but the method is not very sensitive. Further, in the presence of D2EHPA, or similar extractants, this approach is not suitable because the D2EHPA forms an extractable species and interferes.

Perhaps the most promising approach to the determination of TBP in aqueous raffinates is by forming an extractable complex with a metal ion, and determining the metal in the extracted phase. For example, a modification of the method of Nikoleav[108], in which the uranyl nitrate - TBP complex, $(UO_2)(NO_3)_2 \cdot TBP$, is formed in aqueous solution, extracted into a suitable organic solution, and the extracted uranium determined colorimetrically by a reagent such as Arsenazo or bromo-pyridylazo-diethylaminophenol. Alternatively, the TBP extracted into the organic phase (as a metal-TBP complex) may be determined by gas chromatography.

5. Modifiers

Reagents of concern here are aliphatic alcohols - especially isodecanol and 2-ethyl hexanol - and TBP. These reagents are used as modifiers in amine and alkylphosphoric acid solvent systems.

Many methods have been reported for the determination of monoaliphatic alcohols in aqueous solution. Thus, Chalov and Volskaya[167] converted ethanol to ethyl nitrate by reaction with nitrous acid, formed an azo dye and determined this colorimetrically. Parker[168] used a similar method, which was later modified by Wellington[169] for micro determination of monohydric aliphatic alcohols.

Oxidation of alcohols with various oxidants, and subsequent determination by spectrophotometry, have been reported. Ginther and Finch[170] oxidized isopropanol to acetone with potassium persulphate, followed by reaction of the acetone produced with alkaline salicylaldehyde to form the orange-red dihydroxybenzal acetone. Other oxidizing agents such as dichromate have been used, but the colors produced by this reagent has necessitated distillation of the acetone prior to its determination[171-173] or limiting of the method of acetone determination because of this color[174].

Spectrophotometric determination of aliphatic alcohols employing ceric ammonium sulphate as reagent have been reported[175, 176]. These are not applicable to the microgram range. Other

colorimetric methods involve reactions of alcohols with vanillin or p-dimethylaminobenzaldehyde[177,178], chromotropic acid after oxidation[179], and phenylhydrazine[180].

Acetylation of primary and secondary alcohols, followed by hydroxamation, was used by Gutnikov and Schenk[181]. Volumetric methods for the determination of alcohols in aqueous solution have been reported, based on the back titration of excess oxidant ($KMnO_4$, xenon trioxide, ceric sulphate) after oxidation of the alcohol[182, 183]. Konishi et al.[184] have reported a procedure based on the oxidation of alcohol with excess bromine chloride, the excess being titrated iodometrically. Gas chromatography has also been used to determine alcohols in aqueous solutions[185].

Probably the procedure most studied for the determination of aliphatic alcohols in aqueous solution is that involving the formation of a red extractable vanadium(V) oxinate - alcohol complex[186,190]. Other vanadium complexes also give rise to red colors in the presence of alcohols, and have been suggested for the determination of alcohols[190]. But while these methods are sensitive and accurate for the determination of alcohols in water, they are not directly applicable to the determination of alcohols in solvent extraction raffinates. The reason for this is that raffinates contain trace or major amounts of metals which form extractable colored complexes with oxine, and consequently interfere. Separation of the alcohol is thus required prior to its determination. This same problem of interferences is common to

all the methods, except perhaps for the case of gas chromatography.

There does not appear to be any satisfactory method available for the determination of monohydric aliphatic alcohols, in the ppm range, in raffinates from solvent extraction processes.

The same situation obtains in the case of TBP, when it is used as a modifier in the D2EHPA solvent system. The method of forming an extractable metal - TBP species is inapplicable since D2EHPA would (almost certainly) form a similar metal species and extract with the TBP - metal species. If the TBP could be extracted from the aqueous phase into an organic solvent, it could probably be determined by gas chromatography. In this case, any D2EHPA co-extracted would not interfere.

6. Diluents

The determination of kerosene-type diluents in aqueous solution presents many problems to the analyst. These materials are fractions of crude oil, and can contain many different types of hydrocarbons, ranging from aliphatic to aromatic. Further, variations in composition of the diluent, even though small, could affect both the analysis and the extraction of metals.

Determination of kerosenes, or similar materials, in aqueous solutions in the ppm range has been investigated by several workers[191-196]. The method described by Lee and Walden[197] is satisfactory for the determination of kerosene (Shell 140 Flash Naphtha) in aqueous solution provided no other organic compounds are present. Almost all organic materials give a turbidity under

the conditions of the method. Thus, the method is not suitable for the determination of kerosene in raffinates from solvent extraction processes.

There are apparently no reported methods for the determination of kerosene-type diluents, in the ppm range, in aqueous raffinates containing similar amounts of other organic reagents.

THE DETERMINATION OF METALS

Determination of Metals in Extracts

Many investigations into the extraction of metals by various solvents are carried out without analysis of the organic phase for metal content. It is generally assumed that analysis of the aqueous phase is adequate, and the concentration of metal in the organic phase is the difference between the metal concentration in the feed and raffinate, corrected for the phase ratio. While this is quite satisfactory under strictly controlled extraction conditions, for pure solutions containing only one metal, and where a volume change is known not to occur, this approach can lead to erroneous conclusions if volume changes do occur. In some solvent systems, the changes in volume of both the organic and aqueous phases are quite significant. For example, in the extraction of zirconium from strong (8M) nitric acid solutions using a TBP-kerosene solvent, the volume change in the organic phase can be as much as 40% (increase)[115].

The need for analysis of the organic phase for metals also arises when leach liquors, rather than pure solutions, are used. Leach liquors usually contain a number of metals, in concentrations varying from ppm to several g/l. In some systems, a build-up of a metal in the solvent phase, as a result of recycling of the solvent and failure to strip the particular metal, may occur. Analysis only of the raffinate may not show this build-up. The problem will then only become evident when the extraction of the desired metal falls off, that is, when the efficiency of the extraction becomes sufficiently low to give high raffinate losses of the metal being extracted. Analysis of the solvent is also required if metallurgical balances are to be determined. For these several reasons, analysis of the solvent for metals is considered to be necessary at some point in the process.

Conventional methods for the analysis of metals, such as volumetric, gravimetric, colorimetric and so on, require the separation of the metal from organic compounds. In the analysis of solvents this usually entails decomposition of the solvent with acids, alkalis, thermal methods, etc. But because of the nature of many of the constituents of solvents used in commercial solvent extraction processes, this is not too easy. Most reagents are long chain organic compounds which are not readily broken down by aqueous attack, and the procedure usually entails fuming with powerful oxidizing agents, which is time consuming

not particularly suited to routine analysis. Removal of solvents by burning in magnesium oxide or similar material may be suitable for small volumes (a few ml) of solvents, but is subject to mechanical loss of inorganic materials.

Stripping of the metal from the organic phase by a suitable aqueous solution, and analysis of the aqueous solution for the metals of interest, is used frequently. Provided that complete stripping of the metal can be accomplished, this approach can be rapid and accurate. One problem to watch is the effect of soluble organic material on the methods used for metal analysis in the strip solution, especially if organic materials interfere in subsequent analyses. It may be necessary to remove the soluble organics by evaporation and fuming, or some similar method, before the analysis. Effects of soluble solvents on instrumental methods, such as atomic absorption, should be investigated.

Having obtained the metal in solution, free from organic material, it has to be analysed by some method. The whole process of decomposition of the solvent, followed by analysis of the metal, is time consuming, and in a process laboratory is expensive.

Probably the fastest and cheapest method (after the initial instrument cost) for the determination of metals in solvent samples is by X-ray fluorescence. While the capital outlay for such instrumentation is high, this is offset by the speed and accuracy of this method, not only for solvent samples but also for most aqueous samples.

Like any analytical method which employs instrumentation, x-ray fluorescence requires calibration by known standards. Thus solutions of solvents containing known concentrations of metals must be prepared. These standards must then be analysed by methods known to be suitable for the determination of the particular metals in organic solutions.

Another approach which may be considered for the determination of metals in solvents is atomic absorption. However, the problems of the effects of the organic materials on the flame properties, burner coking, nebulization, and so on, need to be thoroughly investigated for a particular solvent system. Most solvents when loaded with metals are quite viscous, and entirely unsuitable for analysis by atomic absorption. If the metal concentration is sufficiently high, considerable dilution of the sample with an organic liquid, such as methylisobutyl ketone or another diluent which is suitable for use in AA, can be used. These factors would depend on the particular solvent system, and would need to be investigated for that particular system.

ANALYSIS OF RAFFINATES AND STRIP LIQUORS

The determination of metals in raffinates, strip liquors, and other aqueous solutions from solvent extraction processes can be accomplished by many methods. These will not be covered here, as many excellent texts and papers are available which discuss analysis of metals in aqueous solutions. The analyst should,

however, be aware of the fact that all these solutions will contain organic materials from the solvent, which may affect the analysis. For example, raffinates from solvent extraction systems which employ aliphatic carboxylic acids, or methyl isobutyl ketone, may contain several g/l of these reagents. Such amounts could have a considerable effect on some methods of analysis for metals.

CONCLUSIONS

The analytical methods given in this monograph are not intended to cover all eventualities, but are presented as a guide to the solution of analytical problems in solvent extraction processing. Some will undoubtably need to be modified for specific applications.

Only those methods which require a minimum of equipment and operator skill have been considered, since these are more applicable to use in plant control laboratories. More sophisticated methods, employing instrumentation can no doubt be applied successfully to the analysis of many of the solutions considered here.

Still to be developed are methods for modifiers and diluents in raffinates, and some of the components of the solvent phase.

Sampling procedures, type of sample container, and other associated problems need to be investigated. Little

work has been reported in this area. Also, on-stream analysis is still another area which has received little attention in the past for application to solvent extraction processing.

There is, therefore, still considerable work to be done in this field of analytical chemistry.

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