Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hasany, S. M. , Umar, Zahid and Ejaz, M.(1979) 'Selective Extraction of Arsenic(III) from Chloride-Thiocyanate Solutions Using Diphenyl-2-pyridylmethane in Benzene', Separation Science and Technology, 14: 5, 431 — 440

To link to this Article: DOI: 10.1080/01496397908058095

URL: http://dx.doi.org/10.1080/01496397908058095

SEPARATION SCIENCE AND TECHNOLOGY, 14(5), pp. 431–440, 1979

Selective Extraction of Arsenic(III) from Chloride-Thiocyanate Solutions Using Diphenyl-2-pyridylmethane in Benzene

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Abstract

The extraction of arsenic(III) with diphenyl-2-pyridylmethane (DPPM) in benzene from chloride–thiocyanate media has been investigated. The variables such as concentration of the acids, thiocyanate, and the extractant have been studied to optimize the extraction procedure. Quantitative extraction of arsenic can be achieved from 10 *M* HCl + 0.1 *M* KSCN medium with 0.1 *M* DPPM in benzene in two to three equilibrations. Possible formulation of the extracted species is $HAsCl_3(SCN)DPPM$. The extraction of arsenic is fairly selective. Useful analytical separations are suggested and some of their possible applications have been illustrated.

INTRODUCTION

Arsenic is one of the toxic elements which occupies an important position in environmental analytical chemistry. The determination of trace amounts of the metal by modern instrumental analytical techniques generally requires its separation/preconcentration. Recent studies (*1*) in this laboratory have revealed the potential of 2-hexylpyridine as a selective extractant for arsenic(III), but the solvent is rather unattractive because of its high vapor pressure. The work reported herein deals with the extraction of arsenic from chloride–thiocyanate solutions by an aryl-

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substituted high-molecular-weight heterocyclic amine, diphenyl-2-pyridylmethane (DPPM), which is completely free from this drawback. The results show that the present reagent can usefully be employed for the separation of arsenic from a number of elements using concentrated hydrochloric acid solutions containing potassium thiocyanate.

EXPERIMENTAL

Reagents and Tracers

DPPM was obtained commercially. The characteristics of this compound are given elsewhere (*2*). Solutions of all the acids used in this study were made from BDH volumetric solution ampules. All other chemicals used were either of AnalaR grade or of the highest purity available. ^{76}As was obtained by neutron irradiation of specpure arsenic oxide in the research reactor PARR-I of this institute. All other tracers employed in this study were either prepared from neutron irradiations or were purchased commercially or from parent–daughter separations. The radiochemical purity of the used tracers was usually checked by γ-spectrometry using a 30 cm^3 Ge(Li) detector coupled with a Nuclear Data Model ND-4410 computerized analyzer. The purity of β-emitters was checked by their absorption curves.

Extraction Procedure

Potassium thiocyanate was added to obtain the desired concentration to 1 ml of the mineral acid containing a tracer of arsenic (^{76}As) or the test element. The aqueous phase was equilibrated with an equal volume of 0.1 *M* DPPM solution in benzene for 5 min. (Preliminary studies showed that equilibrium is achieved within 1 min.) After centrifugation, two phases were separated and aliquot parts from both the phases were assayed radiometrically to determine the distribution coefficient (*D*) defined as the ratio of the concentration of arsenic in the organic phase to that in the aqueous phase. The equipment used for the radiochemical assay is described elsewhere (*3*).

RESULTS AND DISCUSSION

In preliminary investigations, the extraction of arsenic(III) with 0.1 *M* DPPM solution in benzene was investigated as a function of the concentration of aqueous hydrochloric, nitric, and sulfuric acid solutions, and no extraction was observed except in concentrated hydrochloric acid media (Fig. 1A) where some extraction was observed which could either be due to the extraction of $AsCl_4^-$ through ion association or due to the extraction of a $HAsCl_4$ acid complex salted out by the supporting acid. In nitric acid media, precipitation was observed in the range of 1 to 5 *M* acid concentration and can be explained as due to the aggregation of amine nitrate salts to such an extent that micelles of the pyridine salt molecules settle down in the aqueous phase.

In our previous article (*1*) we found that the extraction of arsenic(III) is generally enhanced by the addition of potassium thiocyanate. To investigate the effect of the concentration of thiocyanate, the partition behavior was studied from several concentrations of hydrochloric acid solutions containing varying amounts of potassium thiocyanate (0.02 to 1 *M*). Figure 1 (A and B) shows the plots of the extraction of arsenic against the concentration of hydrochloric acid solutions containing known amounts of thiocyanate. A comparison of plot 1 in Fig. 1 (A) with other curves of Fig. 1 (A and B) reveals that thiocyanate ions effectively increase the extraction of the element. In almost all cases the extraction of arsenic, which first increases with the increasing acid, passes through a maximum at 4 to 5 *M* concentration and then begins to fall with a subsequent increase above 7 *M* hydrochloric acid. Such an extraction behavior is an indicator of the formation of a number of species in equilibrium in the aqueous phase.

The first increase in the extraction is probably due to the formation of mixed chloride–thiocyanate complexes of the type $AsCl_n(SCN)^{3-n}\cdot(H_2O)_m$ ($n = 1, 2$) which is extracted through solvation (anhydrous or hydrated form). The subsequent decrease could either be explained as due to acid competition for the base or due to the formation of anionic thiocyanate species which are poorly extracted since the base is of the low electronegativity (*2*) ($pK_{BH^+} \simeq 4.41$) and extraction through anionic portion is consequently unlikely to be efficient. The increase in distribution at higher acid concentrations is perhaps due to the formation and extraction of complex metal acids of the type $H_nAsCl_3(SCN)_n$ ($n = 1, 2$) salted out by the supporting acid. In dilute acid solutions the extraction of the metal is not improved by the increasing concentration of thiocyanate, but an appreciable extraction is observed from moderate to higher concentrations of hydrochloric acid. In low acid concentrations the poor extraction, even in the presence of SCN^-, indicates that this ion does not lead to the formation of extractable species. Perhaps under these con-

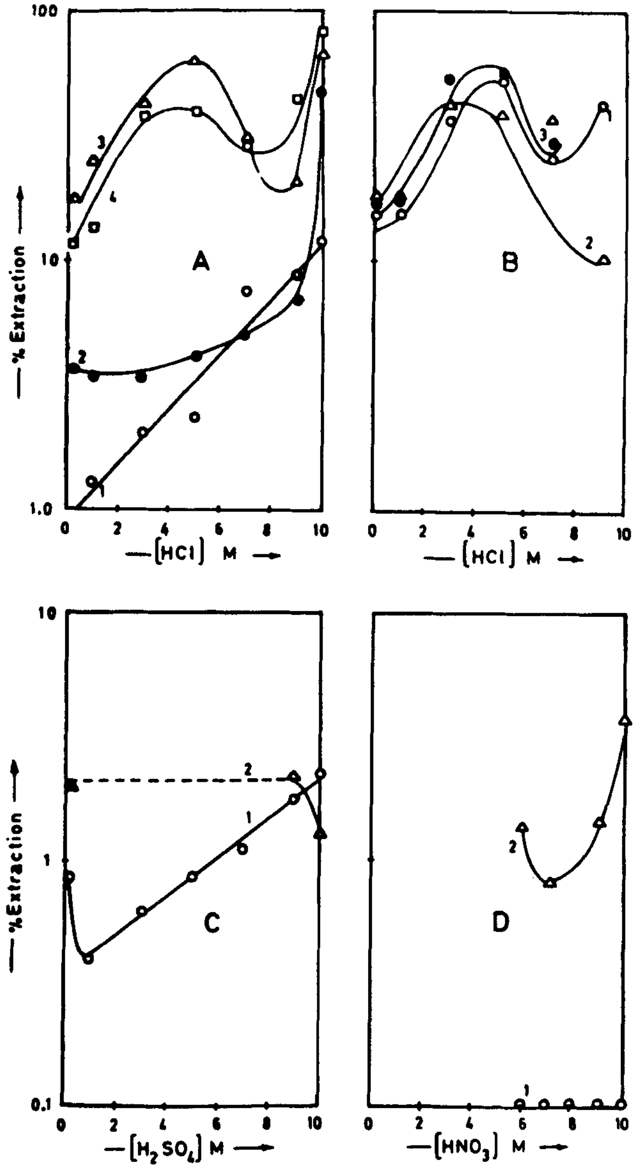

FIG. 1. The dependence of the distribution coefficient on the concentration of the mineral acid solutions containing varying amounts of KSCN with 0.1 *M* DPPM in benzene. A: (1) HCl, (2) HCl + 0.02 *M* KSCN, (3) HCl + 0.05 *M* KSCN, and (4) HCl + 0.1 *M* KSCN. B: (1) HCl + 0.2 *M* KSCN, (2) HCl + 0.5 *M* KSCN, and (3) HCl + 1.0 *M* KSCN. C: (1) H_2SO_4 and (2) H_2SO_4 + 0.1 *M* KSCN. D: (1) HNO_3 and (2) HNO_3 + 0.1 *M* KSCN.

ditions arsenic exists in the form of oxymetal species and thiocyanate does not take part in the complex formation, and as the concentration of supporting acid increases the equilibrium shifts toward the formation of cationic chloride species which lead to the formation of mixed chloride–thiocyanate complexes. Figure 1 (A and B) indicates that the general shape of the extraction curves from hydrochloric acid solutions containing more than 0.05 *M* KSCN is somewhat similar. This indicates that the species extracted in all cases are perhaps the same. However, the plot (Curve 2, Fig. 1A) of the acid variation with 0.02 *M* thiocyanate is different from that of other thiocyanate concentrations. Figure 1(A) shows that most of the metal can be removed from 10 *M* hydrochloric acid containing 0.1 *M* potassium thiocyanate using 0.1 *M* DPPM solution in benzene. A relatively higher concentration of thiocyanate in the aqueous solution decreases the extraction, perhaps due to the competition of thiocyanic acid for association with the base. It can thus be concluded from the data that by using various concentrations of thiocyanate and hydrochloric acid, the distribution behavior of arsenic can be affected in a number of ways while keeping a constant concentration of the metal and the extractant.

The effect of the addition of an optimal concentration of SCN^- (0.1 *M*) to nitric and sulfuric acid solutions on the extraction of arsenic was also checked. The results presented in Fig. 1 (C and D) demonstrate that the addition of KSCN to aqueous nitric or sulfuric acid solutions has no prominent effect on the extraction efficiency. In dilute and moderate concentrations of sulfuric acid (1 to 8 *M*) solutions with 0.1 *M* KSCN, the addition of the reagent caused precipitation. A similar observation was recorded in the case of 0.1 to 5 *M* nitric acid. This suggests that nitric and sulfuric acid media are not suitable for the extraction of arsenic even in the presence of SCN^-. The extraction of arsenic from 10 *M* hydrochloric acid containing 0.1 *M* KSCN is adequate and can be removed quantitatively from the aqueous phase in two to three equilibrations.

The effect of SCN^- on the degree of extraction was also investigated from 10 *M* hydrochloric acid. The thiocyanate concentration was varied from 0.01 to 0.1 *M* at constant (0.1 *M*) DPPM concentration. The results obtained are given in Fig. 2 which shows that the distribution coefficient is proportional to the concentration of thiocyanate. The slope of the curve is 1.06. This indicates a 1:1 molar ratio of arsenic and thiocyanate.

The influence of the concentration of DPPM on the partition of arsenic was examined over the concentration range of 0.001 to 0.2 *M* as shown in Fig. 3. The extraction appears to be independent at low DPPM concentrations up to 0.05 *M*, and a linear region is observed above 0.05 *M* concentra-

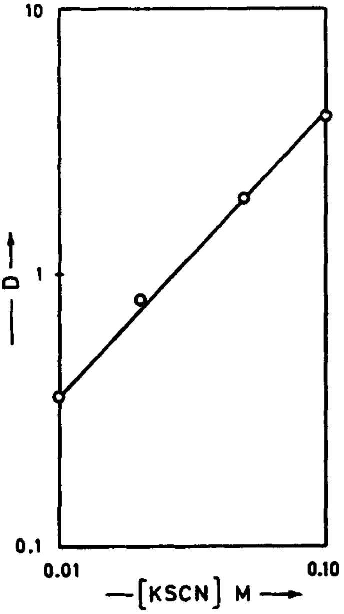

FIG. 2. The variation of the distribution coefficient with the concentration of KSCN from 10 *M* HCl using 0.1 *M* DPPM in benzene.

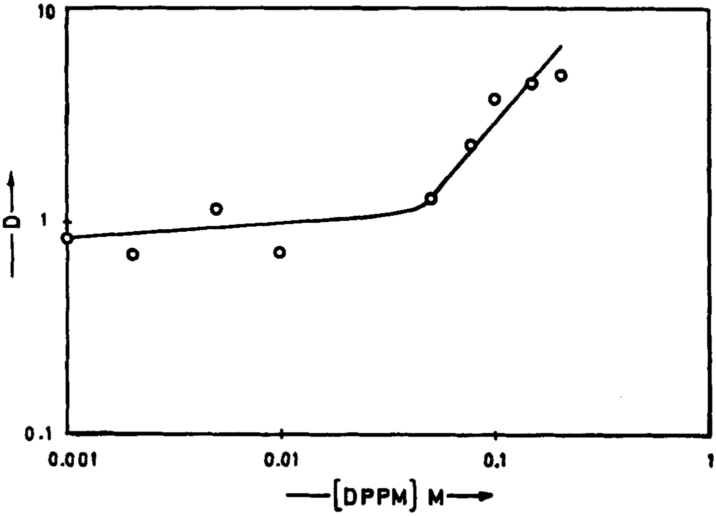

FIG. 3. The effect of DPPM concentration on the distribution coefficient from 10 *M* HCl + 0.1 *M* KSCN solution.

tion where the distribution coefficient increases with increasing ligand concentration. This linear portion of the plot log D vs log [DPPM] has a slope of 1.18. This clearly indicates that each arsenic ion is associated with one molecule of DPPM. The results described above demonstrate that one thiocyanate ion and one molecule of DPPM are involved in the extracted complex. Assuming $HAsCl_3 \cdot SCN$ as the prevailing species of arsenic in hydrochloric acid, the extraction process may be represented by the following sequences:

$$As^{3+} + 3Cl^- \rightleftarrows AsCl_3$$

$$AsCl_3 + HCl + SCN^- \rightleftarrows HAsCl_4/HAsCl_3 \cdot SCN$$

$$HAsCl_3 \cdot SCN + DPPM \rightleftarrows HAsCl_3(SCN)DPPM$$

A study was carried out to determine the influence of a few common anions on the extraction of arsenic from 10 *M* hydrochloric acid in the presence of 0.1 *M* KSCN. The results are reported in Table 1. It is obvious that citrate ions do not affect the extraction whereas acetate, borate, floride, oxalate, phosphate, and thiosulfate partially suppress the extraction. The order of decrease in the extraction of arsenic in the presence of these ions is iodide > floride > acetate > phosphate > thiosulfate > oxalate > borate. Iodide ions affect the extraction significantly and in their presence the extraction was found to be only 18 %. Citrate and borate ions appear to be useful masking agents to remove the interference caused by other elements. However, several other aqueous solutions were also evaluated to determine their ability to strip arsenic from the organic phase. The studies have shown that 1 *M* hydrochloric and 10 *M* nitric acid are

TABLE 1

The Effect of Various Anions (1 mg/ml) on the Extraction of As(III) with DPPM in Benzene from Chloride–Thiocyanate Medium

Added as	*D*	% *E*
Nil	3.87	79.4
Sodium citrate	3.97	79.9
Sodium borate	3.14	75.9
Sodium oxalate	2.06	67.3
Sodium thiosulfate	1.95	66.0
Sodium phosphate	1.82	64.6
Sodium acetate	1.80	64.2
Sodium floride	1.46	59.5
Potassium iodide	0.22	18.4

suitable media to back-extract more than 99% of the metal in a single stripping operation.

To check the selectivity of the extraction of arsenic(III), the distribution coefficients of several other elements were determined under the optimal conditions. The data are recorded in Table 2. It appears from Table 2 that Ga(III) is extracted almost quantitatively while the extraction of most of the other elements is poor. Arsenic can be selectively separated from

TABLE 2

Distribution Coefficients and Separation Factors of Different Elements with Respect to As(III) from 10 *M* HCl Containing 0.1 *M* KSCN by 0.1 *M* DPPM in Benzene

Ion	Concentration of element, *M*	Distribution coefficients	Separation factors
As(III)	10^{-4}	3.87	—
Na(I)	10^{-4}	0.00	$>10^{4}$
K(I)	10^{-4}	0.00	$>10^{3}$
Br(I)	10^{-4}	0.01	282
Cs(I)	10^{-6}	0.00	$>10^{3}$
Tl(I)	10^{-5}	0.05	77.2
Mn(II)	10^{-5}	0.02	188
Co(II)	10^{-4}	0.24	16.2
Ni(II)	10^{-3}	0.02	166
Cu(II)	10^{-5}	0.07	53.3
Zn(II)	10^{-4}	0.21	18.3
Sr(II)	10^{-5}	0.00	$>10^{3}$
Cd(II)	10^{-5}	0.17	22.6
Ba(II)	10^{-6}	0.00	$>10^{3}$
Cr(III)	10^{-5}	0.02	167
Ga(III)	10^{-3}	250	0.01
Y(III)	10^{-4}	0.00	$>10^{3}$
La(III)	10^{-4}	0.00	$>10^{3}$
Pm(III)	10^{-4}	0.00	$\sim 10^{3}$
Eu(III)	10^{-4}	0.00	$\sim 10^{3}$
Au(III)	10^{-4}	0.00	$\sim 10^{3}$
Ti(IV)	10^{-6}	0.00	$\sim 10^{3}$
Sn(IV)	10^{-4}	0.30	13.0
Hf(IV)	10^{-4}	0.36	10.7
Ce(IV)	10^{-5}	0.01	395
Pt(IV)	10^{-4}	0.30	12.8
Pb(IV)	10^{-5}	0.69	25.6
Th(IV)	10^{-4}	0.05	77.1
Sb(V)	10^{-5}	2.08	1.9
U(VI)	10^{-5}	3.71	1.0

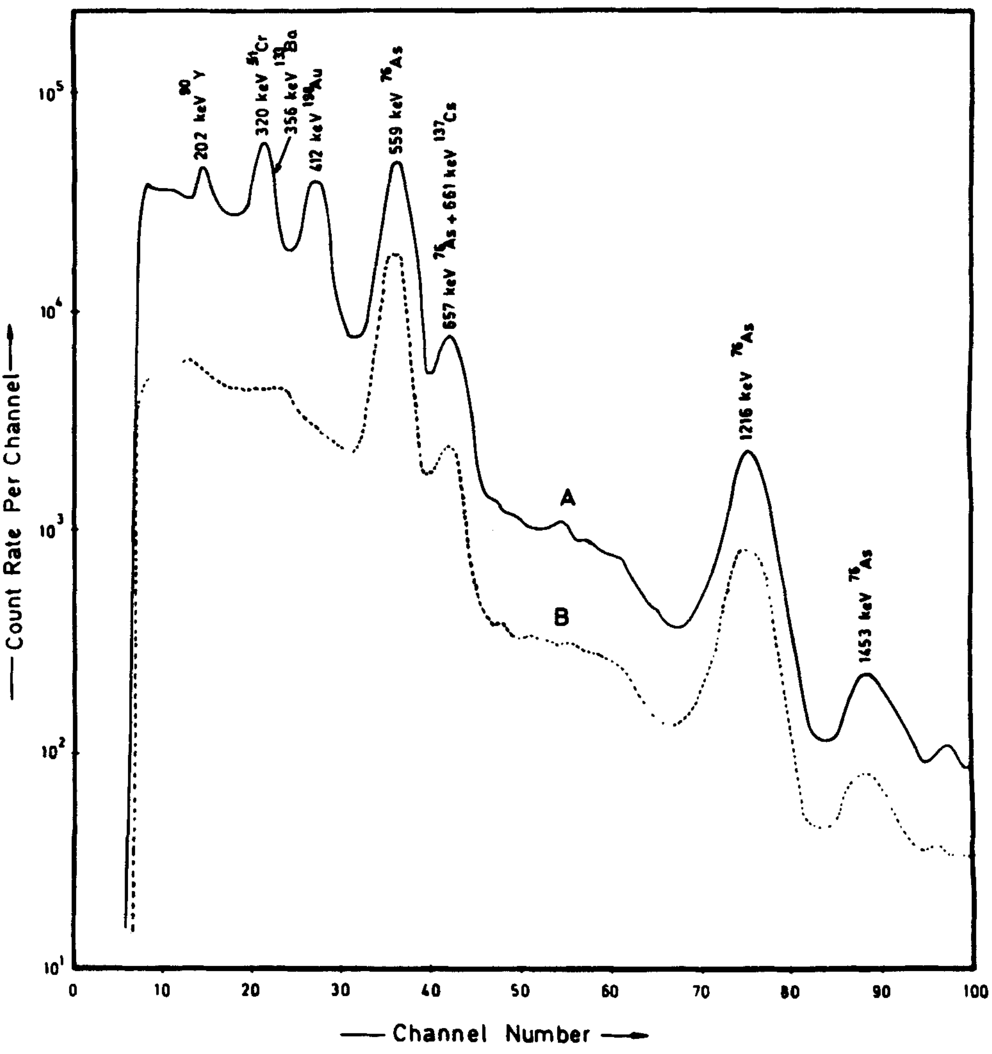

FIG. 4. The gamma spectra of the mixture of radiotracers before (A) and after (B) separation.

several other elements. To check the reliability of the extraction separation procedure, a synthetic mixture containing ^{51}Cr, ^{90}Sr–^{90}Y, ^{133}Ba, ^{137}Cs, and $^{198+199}Au$ with 7.5 mg carrier of each of these elements and ^{76}As (tracer amounts) was subjected to the extraction. Figure 4 shows the gamma spectra of the mixture before and after separation. It is evident that arsenic is cleanly separated from all these elements, with no contamination from any one of them noted.

The separation of arsenic from different elements can be usefully employed in the isolation of cyclotron-produced short-lived isotopes of bromine for medical uses from arsenic-irradiated targets. In addition, this procedure can also be used to separate arsenic from a number of associated metals, in particular chromium (*4*, *5*) and nickel (*6*), in a number of modern analytical techniques, e.g., atomic absorption spectrometry.

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Received by editor September 26, 1978