LIQUID–LIQUID EXTRACTIONS WITH METAL DIETHYLDITHIOCARBAMATES AS REAGENTS

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The liquid-liquid extraction of about twenty ions with metal diethyldithiocarbamates in chloroform from citrate buffers of pH 2–6 and the most common inorganic acids has been studied. Several backextraction reagents have been examined: hydrochloric acid (1–12M), dilute nitric acid saturated with bromine and a mixture of concentrated hydrochloric acid and hydrogen peroxide. A short review of metal diethyldithiocarbamates as extraction reagents and a mathematical model for these extractions are also included.

Introduction

Diethyldithiocarbamates are widely used as metal ion extraction reagents for the separation of many elements.[1-13b] There are many reasons for this: (1) The diethyldithiocarbamate anion [C_2H_5)$_2$ NCS(I), hereinafter denoted by DDC] reacts with most of the elements from the group IVB to VIA of the periodic table, but not with those of IA to IIIB and the rare earths;[10] (2) the diethyldithio-carbamates formed are practically insoluble in water, but they dissolve readily in organic solvents;[14-16] (3) this solubility is so high that even milligrams of most elements can be easily extracted; (4) many elements are extracted from a very wide acidity range, from mineral acids to alkaline solutions

All these advantages make DDC the reagent of choice for group separations. This also means that the selectivity is poor. It can be increased by acting upon the aqueous phase (acidity, masking agents, oxidation state of the elements), by selecting the extraction reagent [NaDDC, (C_2H_5)$_2$ NH$_2$ DDC, M(DDC)$_n$ (M = metal)], and by the way of adding the reagent: directly in the aqueous phase (NaDDC) followed by the organic solvent or dissolved in the organic phase [(C_2H_5)$_2$ NH$_2$ DDC, M(DDC)$_n$]. The reagent NaDDC is not soluble in organic solvents which are not miscible with water, and therefore must be employed in aqueous solution.

The use of $M(DDC)_n$ dissolved in organic solvents also has the advantage of an extended shelf life.[17] Solutions of $(C_2H_5)_2NH_2DDC$ in organic solvents and those of NaDDC in water must be prepared every day. Furthermore, in an actual extraction, the half-life of NaDDC in aqueous solutions of pH 1–3 is about 10 s,[18,19] and as a result, the utilization of this reagent is limited to higher pH values. Extractions with $(C_2H_5)_2NH_2DDC$ or $M(DDC)_n$ can be performed even from 5M mineral acid solutions; both reagents are very stable when shaken with acid solutions.[17,20]

Systematic studies have been published of $M(DDC)_n$ as extraction reagents. They may be distributed in several groups: (1) displacement of M from $M(DDC)_n$ by an excess of another ion in the aqueous phase;[21-23] (2) extractive titration with $Zn(DDC)_2$;[24] (3) extractions with $M(DDC)_n$ in excess relative to the ion being extracted.[25-27]

The reviews of HULANICKI[6] and SPIVAKOV and ZOLOTOV[28] include many examples of all the three preceeding groups. Recent applications of $M(DDC)_n$ as extraction reagents are shown in Table 1.

The extraction constants of many DDC are known.[50,78] New determinations of extraction constants (all using chloroform or carbon tetrachloride as the organic phase) can be found in the following references: Cd, Pb, and Zn;[17] As, Bi, Cd, Hg and Fe;[79] Mn, Pb, Tl, and Zn;[80] Co, Fe, and Zn;[81] Tl[66] and Po.[82] The extraction

Table 1
Literature survey of extractions by $M(DDC)_n$

Extraction reagent	Metals extracted
Ag(DDC)	Hg[29]
As(DDC)$_3$	As[30], Cu[31]
Bi(DDC)$_3$	Ag[32,33], Au[32,33], Bi[34], Cu[32,33,35-38], Po[34]
Cd(DDC)$_2$	Bi[39], Cu[39], Mo[38]
Cu(DDC)$_2$	Ag[40], Au[41,42], Hg[43-45], Pd[46-48], Pt[41]
H(DDC)	Cd[49,50], In[50], Pb[51], Zn[50]
Hg(DDC)$_2$	Cu[52]
Ni(DDC)$_2$	Au[53], Hg[36,54,55]
Pb(DDC)$_2$	Ag[56], Au[57], Cu[31,56-59], Hg[56,57,60,61], Pb[62,63]
Sb(DDC)$_3$	Cu[64], Sb[30]
Te(DDC)$_2$	Cu[65]
Tl(DDC)	Cd[66], Co[66], Fe[66], Tl[67], Zn[66]
Tl(DDC)$_3$	Tl[67]
Zn(DDC)$_2$	Ag[68,69], As[36,38,70], Au[13,71,72], Bi[73], Cd[36,37,49,55,69], Cu[13,31,35,69-71,74], Hg[13,70,71,75,76] Mo[36,64], Pb[51], Sb[70], Se[77]

constants of the mixed complexes $As(DDC)_2Cl$, $Bi(DDC)_2Cl$, $Bi(DDC)Cl_2$, $Cd(DDC)Cl$,[79] and $Au(DDC)Cl_2$[83] have been also determined.

The knowledge of the extraction constants is of paramount importance in the design of any liquid — liquid extraction procedure. Some mathematical expressions have been obtained for extractions with $H(DDC)$[50] and $M(DDC)_n$.[25,52,81,84,85]

However, it is not always possible to apply the derived expressions to the problems encountered in an actual extraction. In some cases, the extraction constants are not known (i.e. Mo(VI), Sb(III), Se(IV), Te(IV), Tl(III); in others, the extraction is performed under conditions far from ideal. Furthermore, kinetic factors play an important role (i.e. $Co(DDC)_3$, $MoO_2(DDC)_2$, $Ni(DDC)_2$).

The present work was undertaken in order to study some $M(DDC)_n$ in chloroform as extraction reagents for metals by making use of radioactive tracers.

Experimental

Reagents

The different $M(DDC)_n$ (M = Hg(II), Ni(II), Cu(II), Bi(III), In(III), Pb(II), Cd(II), Zn(II), Tl(I), H(I)) were prepared as described previously.[25] Detailed working procedures for preparing $Zn(DDC)_2$ have also been given.[27,69] The solid $M(DDC)_n$ were weighed to prepare $1.70 \cdot 10^{-3}$ M solutions in chloroform, which were stored in dark bottles. The solutions of $Cd(DDC)_2$ and $Zn(DDC)_2$ are stable for at least 40 days.[17]

To prepare a solution of HDDC $3.4 \cdot 10^{-3}$ M in chloroform, shake equal volumes of $Zn(DDC)_2$ $1.70 \cdot 10^{-3}$ M in chloroform and 2M HCl for 30 s in a separatory funnel. Let the mixture stand for 1 min and then, drain the organic phase into

Table 2
Composition of the citrate buffers

Buffer	pH	Concentration (molarities)	
		$C_6H_8O_7 \cdot H_2O$	$Na_3C_6H_5O_7 \cdot 2H_2O$
B1	2.13	$6.67 \cdot 10^{-2}$	0
B2	2.93	$4.93 \cdot 10^{-2}$	$8.70 \cdot 10^{-3}$
B3	4.05	$2.86 \cdot 10^{-2}$	$1.90 \cdot 10^{-2}$
B4	5.05	$1.41 \cdot 10^{-2}$	$2.63 \cdot 10^{-2}$
B5	6.14	$3.53 \cdot 10^{-3}$	$3.16 \cdot 10^{-2}$

another separatory funnel which contains the aqueous phase to be extracted. Perform the extraction immediately. The solution of HDDC in chloroform is not stable.[17]

Buffered solutions were prepared by dissolving citric acid and sodium citrate in water as shown in Table 2.

Solutions of the metals under investigation marked with an appropriate gamma-emitting isotope were prepared, and contained 1 mg/ml of metal.

Apparatus

Extractions were done in 250 ml separatory funnels[77] at room temperature (21 °C) on a shaking machine with an amplitude of 6 cm and a frequency of 6.6 s^{-1}. The phases were then separated by decantation.

Counting was done with a well-type NaI(Tl) crystal linked to a single-channel γ-spectrometer.

Liquid – liquid extractions

The aqueous phase was 100 ml of acid or a buffered citrate solution (Table 2) and contained 100 μg of the ion under investigation, and the organic phase was 30 ml of $1.7 \cdot 10^{-3}$ M $M(DDC)_n$ of $3.4 \cdot 10^{-3}$ M H(DDC) in chloroform. The shaking time was 2–10 min. Aliquots of each phase were then taken for the measurement of the radioactivity.

Whenever necessary, a $HClO_4$ solution or a NaOH solution was added before the extraction to neutralize the alkali or the acid incorporated with the ion. This volume was always smaller than 1 ml.

Backextractions

The backextraction using different reagents was studied on organic extracts prepared as follows: 100 ml of acid ($\leqslant$0.1M) or a buffered citrate solution (Table 2) containing 100 μg of the ion to be investigated was extracted twice with 30 ml of $1.70 \cdot 10^{-3}$ M $Zn(DDC)_2$ or $3.4 \cdot 10^{-3}$ M HDDC for 2–10 min. For the backextraction with HCl, a washing with 10 ml of chloroform was substituted for the second extraction. Both organic extracts were combined. The backextraction was performed immediately.

Backextraction with HCl. The organic phase (40 ml) was shaken with 10 ml of 1–12.2M HCl for 2 min.

Backextraction with bromine. The organic phase (60 ml) was shaken with 5 ml of 0.1M HNO_3 saturated with bromine for 30 sec, set aside for 5 min and shaken again for 2 min.

Backextraction with HCl + H_2O_2. To the organic phase (60ml), 1 ml of 12.2M HCl and 0.20 ml of 30% H_2O_2 were added and the mixture was shaken by hand for several seconds. It was set aside for 5 min (with the separatory funnel stopped to avoid losses of chlorine), shaken for 2 min, set aside at least for 10 min, diluted with 9 ml of water and shaken again for 30 seconds.

In all the cases, aliquots of each phase were taken for the measurement of the radioactivity.

Results and discussion

Extraction by M(DDC)$_n$ from the citrate buffers

The experimental results are shown in Table 3, where the $M(DDC)_n$ reagents are listed in decreasing order of the experimentally found extracting power. Arsenic(V), Sb(V), Se(VI), and Te(VI) were not extracted by HDDC (<0.1%, 10 min) from any citrate buffer and they were not further investigated. None of the ions listed was extracted by $Hg(DDC)_2$ (<0.1%, 10 min). Only Hg(II) was extracted by $Ni(DDC)_2$ and $Cu(DDC)_2$ over the full range (>99.5%, 2 min); the other ions were not extracted (<0.1%, 10 min). In the cases where there is neither complete extraction nor lack of extraction over the entire range, the fraction extracted changes monotonically between the given limits, with the exception of Co(II), Zn(II), and Fe(III) with Tl(DDC) and Fe(III) with HDDC.

Some ions showing low metallic character are poorly extracted even by HDDC from all the solutions. Adding 15 ml of 10M HCl to 100 ml of the citrate buffers B1 – B5 allows quantitative extraction (>99.5%) of As(III), Mo(VI), and Se(IV) with $Zn(DDC)_2$ (2 min, but 10 min for Mo(VI)). Again, no extraction (<0.1%, 2 min) was found for As(V), Sb(V), Se(VI), and Te(IV) with the same reagent. Although not actually tested, quantitative extraction is expected for Bi(III), Cu(II), Hg(II), Sb(III), and Te(IV) under the same conditions.

It is clear that the extraction ability of a given $M(DDC)_n$ must be related to its capability to release DDC, the extracting agent. This can be calculated with

Table 3
Extraction by $M(DDC)_n$ from the citrate buffers

Ion aqueous phase	Extraction reagent, M in $M(DDC)_n$						
	Bi(III)	In(III)	Pb(II)	Cd(II)	Zn(II)	Tl(I)	H(I)
Hg(II)	Q(2)	Q(2)	Q(2)	Q(2)	Q(2)	Q(2)	Q(2)
Cu(II)	Q	Q–72	Q(2)	Q(2)	Q(2)	Q(2)	Q(2)
Bi(III)	NI	Q(a)	Q	Q	Q(2)	Q	Q(2)
Pb(II)	N–11	NI	NI	Q(2)	Q(2)	NI	Q(2)
In(III)	N–0.4	NI	98–8	Q–38	Q(a)	Q(a)	Q
Cd(II)	N–7	0.8–30.	23–89	NI	Q(2)	Q	Q(2)
Sb(III)	N	12–N	94–N	Q–1	Q	Q	Q
Te(IV)	N	6–0.2	69–0.2	Q–0.2	Q(a)	Q	Q(2)
Se(IV)	N	N(d)	N(f)	53–N	Q–N	Q–0.2	Q–35
Tl(I)	N	N(e)	N(e)	N–3	2–68	NI	5–Q
As(III)	N	N	N(f)	N(g)	67–N	NI	Q–63
Co(II)	N	N	N	0.6–N	14–37	38–27	Q(b)
Zn(II)	N	N	N	2–1	NI	78–94	Q(c)
Fe(III)	N	N	N	N(d)	10–0.2	15–0.4	56–40
Mo(VI)	N	N	N	N	N(g)	7–N	13–0.2
Mn(II)	N	N	N	N	N	N	N–25

Conditions: 10 min of shaking time.

Keys: N — No extraction (≤0.1%) over the entire range of citrate buffers.
Q — Quantitative extraction (≥99.5%) over the entire range of citrate buffers.
Q(2) — Like Q (2 min shaking time).
NI — Not investigated.
98–8 — Fraction (%) extracted from B1 – fraction (%) extracted from B5. (B stands for the buffers of Table 2).
(a) — 96% extracted from B5.
(b) — 76% extracted from B1.
(c) — 93% extracted from B1.
(d) — 0.4% extracted from B1.
(e) — 1% extracted from B5.
(f) — 2% extracted from B1.
(g) — 4% extracted from B1.

the fundamental relationships

$$K_e = \frac{[M(DDC)_n]_o\,[H]^n}{[M]\,[HDDC]_o^n}, \tag{1}$$

$$\alpha = \frac{[M']}{[M]} , \tag{2}$$

$$K_{HDDC} = \frac{[H] [DDC]}{[HDDC]} , \tag{3}$$

$$p_{HDDC} = \frac{[HDDC]_o}{[HDDC]} , \tag{4}$$

$$p_{M(DDC)_n} = \frac{[M(DDC)_n]_o}{[M(DDC)_n]} , \tag{5}$$

where K_e – extraction constant of $M(DDC)_n$,
α – Ringbom coefficient of side reactions,[86]
K_{HDDC} – acid dissociation constant of HDDC,
p_{HDDC} – distribution constant of HDDC,
$p_{M(DDC)_n}$ – distribution constant of $M(DDC)_n$.

The subscript "o" denotes the organic phase.

The mass balances of M and DDC are

$$[M']V + [M(DDC)_n]_o V_o + [M(DDC)_n]V = C_M V, \tag{6}$$

$$n[M(DDC)_n]_o V_o + n[M(DDC)_n]V + [HDDC]_o V_o + [HDDC]V +$$

$$+ [DDC]V = C_{DDC}V_o \tag{7}$$

where C_M – total initial concentration of M taken in the aqueous phase,
C_{DDC} – total initial concentration of DDC (as $M(DDC)_n$) in the organic phase.

The volumes of the organic and the aqueous phase are V_o and V, respectively.

By combining Eqs (1) – (7), an equation which allows us to calculate [DDC] is obtained (if $\dfrac{V_o}{V} \, p_{M(DDC)_n} \gg 1$)

$$\frac{K_e p_{HDDC}^n}{K_{HDDC}^n} \, \frac{V_o}{V} \, U[DDC]^{n+1} + \frac{K_e p_{HDDC}^n}{K_{HDDC}^n} \, \frac{V_o}{V} \left(nC_M - C_{DDC}\frac{V_o}{V} \right) \, \cdot$$

$$[DDC]^n + \alpha U[DDC] - \alpha C_{DDC} \, \frac{V_o}{V} = 0 \tag{8}$$

$$\text{where} \quad U = 1 + \left(1 + \frac{V_o}{V} \, p_{HDDC} \right) \frac{[H]}{K_{HDDC}} \tag{9}$$

Equation (8) is identical with Eq. (1) in Reference.[81]

Figure 1 shows the pDDC vs pH curves calculated with Eq. (8) for the $M(DDC)_n$ listed in Table 3. The following constants were employed:[50] lg p_{HDDC} = 3.37, lg K_{HDDC} = –3.35, lg K_e = 26.9 [Hg(II)], 12.8 [Cu(II)], 15.7 [Bi(III)], 7.94 [Pb(II)], 9.90 [In(III)], 5.56 [Ni(II)], 5.77 [Cd(II)], 2.39 [Zn(II)], and 0 [Tl(I)]. The Ringbom coefficient, α, was always taken as 1. When $\alpha > 1$, the curves are displaced to lower pDDC values; their limiting value is the curve for HDDC. If the system

contains M in excess to the stoichiometry $M(DDC)_n \left(nC_M > C_{DDC} \, \dfrac{V_o}{V} \right)$, the

curves are shifted to higher pDDC values. The influence of α and of an excess of Zn in the case of $Zn(DDC)_2$ is shown in Fig. 2. All the curves show a minimum pDDC value for pH >7.5. Above this pH, pDDC is independent of the acidity of the aqueous phase, i.e. U in Eq. (9) reaches its limiting value of 1 when [H] goes to 0. All the DDC not bound to M is then in the aqueous phase.

On the other hand, with the help of Eqs. (1)–(4), it is possible to calculate the pDDC limiting values for quantitative extraction ($\geqslant$99.5%) and for no extraction ($\leqslant$0.5%) of a given ion in trace quantities. This is shown in Fig. 3. The same constants as for Fig. 1 were used; for Mn(II), lg K_e = 0.54.[50] Again, α = 1 was supposed. The rectangles contain the pDDC range where the extraction is lower than 99.5% and higher than 0.5%.

By comparison of Figs 1 and 3, the best reagent $M(DDC)_n$ and the best pH can be chosen for a given extraction. The conclusions drawn fit fairly well with the
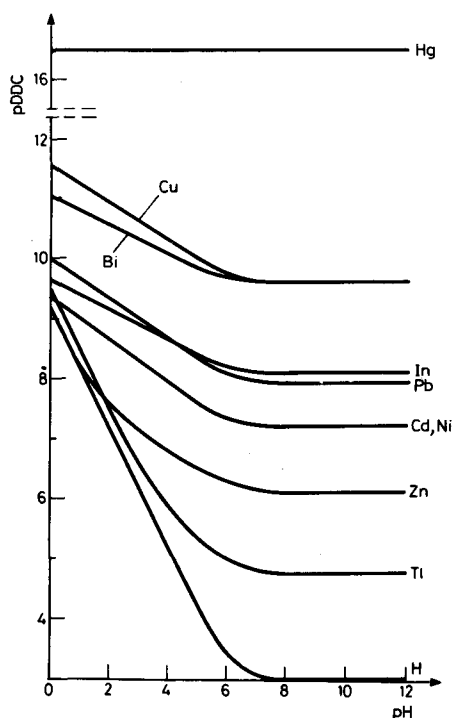
Fig. 1. pDDC-pH curves for different $M(DDC)_n$ (M = Hg, Cu, Bi, etc.). Conditions: $1.7 \cdot 10^{-3}$ M in $M(DDC)_n$ [$3.4 \cdot 10^{-3}$ M in H(DDC)]. V_0 = 30 ml, V = 100 ml
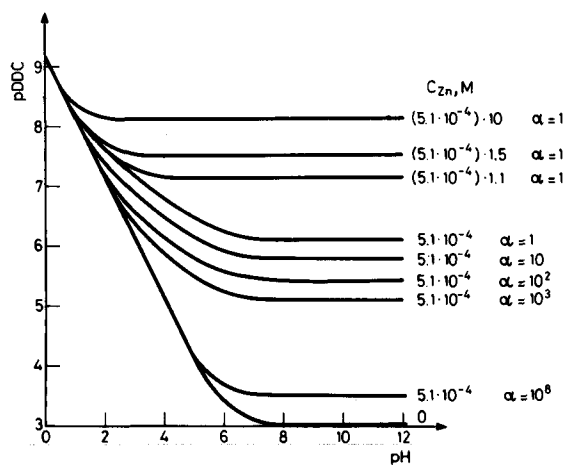

Fig. 2. pDDC-pH curves for $1.70 \cdot 10^{-3}$ M $Zn(DDC)_2$. Conditions: V_0 = 30 ml, V = 100 ml. The concentration, C_{Zn}, $5.10 \cdot 10^{-4}$ M corresponds to the stoichiometric condition
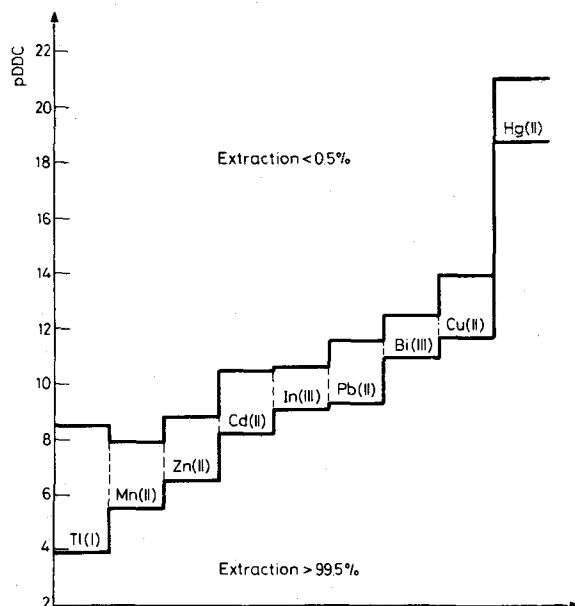
Fig. 3. pDDC regions of total extraction (>99.5%), partial extraction and no extraction (<0.5%) for different ions. Conditions: V_0 = 30 ml, V = 100 ml

experimental results of Table 3. The assumption made of α = 1 in Fig. 1 is certainly not true. Citrate is a relatively mild and not-selective complexing agent.[86,87] Its presence, in general, shifts the pDDC-pH curves to lower pDDC values ($\alpha > 1$ in Fig. 2), thus increasing the extracting power of the $M(DDC)_n$. Simultaneously, this effect is compensated, in general, by lowering the position of the rectangles in Fig. 3.

The reagents $Ni(DDC)_2$ and $Cu(DDC)_2$ show a lower extracting power than expected; this might be due to a kinetic effect, erroneous extraction constants or a too short shaking time, which was arbitrarly limited to 10 min for practical applications.

Extraction by Zn(DDC)₂ from mineral acid solutions

The results are shown in Table 4. The extraction reagent, $Zn(DDC)_2$, is protonated to more than 99% when [H] > 0.4 under these experimental conditions, that is, above this acidity, the same result must be obtained using HDDC

Table 4

Acid concentration ranges for quantitative extraction (>99.5%) with Zn(DDC)$_2$

Ion	Acid range, M						
	HCl	HClO$_4$	H$_2$SO$_4$	HNO$_3$	H$_3$PO$_4$	HF(a)	HF$_4$B
As(III)	0.1 –3	0.1 –3	0.05 –2.5	0.1 –2	0.7 –1.7	1 –5	0.1–3
Au(III)	0.001–1(b) 0.001–3(c)	0.03 –2	0.005 –2.5(b)				
Bi(III)	0.01 –3	0.01 –5	0.005 –2.5	0.01 –1.5			
Cd(II)	0.001–0.01(d)	0.001–0.05	0.0005–0.025		0.0003–0.03		
Co(II)	≥0.1(e)	≥0.5(e)					
Cu(II)	0.001–4	0.001–5	0.0005–2.5	0.001–1	0.03 –1.7	0.1 –5	0.1–5
Hg(II)	0.1 –5	0.1 –5	0.05 –2.5	0.1 –3	0.03 –1.7	0.1 –5	0.1–5
In(III)	0.001–0.01 ≥0.001(e)	0.001–5(f) ≥0.001(e)	0.0005–0.5(g)	0.001–0.1			
Mn(II)							
Mo(VI)	0.01 –5(h)	0.001–5	0.005 –3(i)	0.01 –1.5			
Pb(II)	0.001–0.3 ≥4(e)	0.001–1	0.0005–0.5	0.001–0.5			
Sb(III)	0.1 –5	0.1 –5	0.05 –2.5	0.1 –1	0.03 –1.7	0.1 –3	0.1–5
Se(IV)	0.1 –5	0.1 –5	0.05 –2.5	0.1 –1.5	0.17 –1.7	0.5 –5	0.1–3
Te(IV)	0.1 –5	0.1 –5	0.05 –2.5	0.1 –2	0.03 –1.7	0.1 –5	0.1–3
Tl(I)	≥0.1(e)			≥0.1(e)			
Zn(II)	≥1(e)	≥1(e)					

Conditions: 2 min of shaking time.

Keys: (a) – Two extractions.
(b) – Always 0.10M in HClO$_4$.
(c) – Always 0.50 or 1.0M in HClO$_4$.
(d) – No extraction (<0.1%) from HCl >2M.
(e) – No extraction (<0.1%) under this condition.
(f) – Ten minutes of shaking time.
(g) – 0.0005M–0.05M, 10 min of shaking time; 0.25–0.50M, 30 min.
(h) – Two minutes of shaking time for concentrations up to 1M, 5 min with 2M and 20 min with 5M.
(i) – Two minutes of shaking time for concentrations up to 0.25M, 10 min with 1.5M and 20 min with 3M.

$(3.4 \cdot 10^{-3} M)$ instead of $Zn(DDC)_2$ $(1.7 \cdot 10^{-3} M)$. The former will be preferred if the contamination of the aqueous phase with $Zn(II)$ is objectionable.

The acid concentration ranges given in Table 4 do not exclude quantitative extraction for concentrations outside these ranges. The "upper limit" for the extraction depends on the extraction constant of the ion, the formation of complexes with the anion of the acid and the decomposition of DDC. The first effect is clearly visible with $Co(II)$, $Mn(II)$, $Tl(I)$, and $Zn(II)$. The formation of chloride complexes limits the extraction of $In(III)$ from HCl, as can be seen when compared with the extraction from $HClO_4$. The formation of chloride and sulfate complexes can probably also explain the slow extraction of $Mo(VI)$ from HCl and H_2SO_4. The decomposition of DDC hinders the extractions above 6–7M HCl or $HClO_4$. This limit is much lower (about 2M) with HNO_3 (due to its oxidizing properties), and it is further lowered for those elements with a low extraction rate as $In(III)$,[87a] which needs a long shaking time to be extracted. The extracted of $Au(III)$ by an excess of DDC needs the presence of the perchlorate ion to be quantitative;[24,42,53,88,89] the extracted complex is $Au(DDC)_2 ClO_4$.

Arsenic(V), Sb(V), Se(VI), and Te(VI) are not extracted ($<0.1\%$, 2 min) from $HClO_4$ (0.1–5M) and H_2SO_4 (0.05–2.5M). The same is true for As(V) from HCl (0.1–5M). Selenium(VI) and Te(VI) are more or less reduced to the (IV) state by HCl depending upon the concentration of the acid, the reaction time and the temperature of the solution; this lower oxidation state is extractable over a wide acidity range (Table 4).

Backextraction

The organic extracts to be backextracted were prepared using $Zn(DDC)_2$ for all the cases in which this reagent affords a quantitative extraction of the ion under investigation; HDDC was used in the other cases. The backextraction must follow the extraction without unnecessary delay, especially with the ions which are not quantitatively backextracted, in order to avoid any possible decomposition of the diethyldithiocarbamate in the organic phase; this delay is not important when the backextraction is quantitative.

The results of the backextraction experiments are shown in Table 5. Oxidation of the DDC is the origin of the backextraction with bromine and chlorine (produced by the reaction between HCl and H_2O_2) as they dissolve in chloroform. Simultaneously, some ions reach an oxidation state which cannot react with DDC [As(III) to As(V), Sb(III) to Sb(V)]. With high concentrations of HCl, the DDC is

Table 5

Backextraction of diethyldithiocarbamates

Metal in organic phase	HCl, M												Bromine	HCl + H$_2$O$_2$
	1	2	3	4	5	6	7	8	9	10	11	12		
As(III)	N	N	N	N	N	N							Q	Q
Au(III)	N	N	N	N	N							(a)	N	Q (b)
Bi(III)	N	N	N										Q	Q
Cd(II)		Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q
Co(II)	N	N	N	N	N	N	Q	Q	Q	Q			Q	Q
Cu(II)	N	N	N	N	N	N	N	N	N			(c)	Q	Q
Fe(III)													Q	Q
Hg(II)	N	N	N	N	N	Q	Q	Q	Q	Q	Q	Q	Q (d)	Q
In(III)	N	N	N		Q	Q	Q	Q	Q	Q	Q	Q	Q	Q
Mn(II)		Q	Q	Q	Q	N	N	Q	Q	N		(e)	Q	Q
Mo(VI)	N	N	N	N	N	Q	Q	N	N	Q	Q	Q	Q (f)	Q (g)
Pb(II)				Q	Q	N		Q	Q				Q	Q
Sb(III)	N	N	N	N	N	N	N	Q					Q	Q
Se(IV)	N	N	N	N	N	N	Q	Q	Q	Q	Q	Q	Q	Q
Te(IV)	N	N	N	N	Q	N	Q	Q					Q	Q
Tl(I)	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q (h)	Q
Tl(III)		Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q (c)	Q
Zn(II)	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q

Keys: Q – Backextraction >99.5%.
N – Backextraction ≤0.5%.
Empty – Backextraction between 0.5 and 99.5%.
(a) – The HCl solution was also 1.8M in HClO$_4$.
(b) – Backextraction ≤10%.
(c) – Not studied.
(d) – Backextraction 98–99%
(e) – Shaking time 10 min.
(f) – Backextraction >90%.
(g) – See text.
(h) – Backextraction about 10%.

decomposed at lower concentrations, the replacement of the extracted ion by the proton and the formation of chloride complexes are responsible for the backextraction. As a rule, the higher the extraction constant of the ion, the higher the concentration of the HCl needed to backextract it; this is clear in the series Tl(I), Zn, Cd, Pb, In, Bi, and Cu. But kinetic factors are many times the main determinant (Co, Mn, Mo).

If the aqueous phase resulting from the backextraction is diluted to 100 ml with an acid or a citrate buffer solution, it can again be extracted with an appropriate $M(DDC)_n$. This cycle provides a simple way of enhancing the selectivity of the DDC as extracting agent.

Systematic studies on the backextraction of diethyldithiocarbamates have already been published.[9,27,90]

Backextraction with HCl. Arsenic stays in the organic phase ($\geqslant$95%) for 7–12M HCl, because the beginning of the decomposition of DDC is overlapped by the extraction of As(III) by chloroform as $AsCl_3$.[91,92] It is backextracted ($\geqslant$99.5%) with 12M HCl if 90 ml of water is added after the 2 min shaking period and shaken again for 30 seconds. No oxidation of As(III) to As(V) takes place.

With Au irreproducible results were obtained when HCl alone was used; the fraction backextracted increases with the HCl concentration, ranging from 2–4% with 1M to about 40% with 12M. In the presence of $HClO_4$ the results were reproducible; the fraction backextracted varied in inversely to the concentration ratio of $HClO_4$: HCl, but increases with the concentration of the latter. When the backextration solution was 1.8M in $HClO_4$ and 10M in HCl, 96% of the Au remained in the organic phase; the 4% in the aqueous phase can be quantitatively extracted by shaking with 30 ml of chloroform for 30 seconds. This behaviour of Au is clearly related to the complexes $Au(DDC)_2 ClO_4$ and $Au(DDC)_2 Cl$.[42,88]

Cobalt remained quantitatively in the organic phase over the entire range of HCl. Even if the shaking time was extended to 8 min with 12M HCl, 99.1% stayed in the organic phase. After extraction, Co(II) is oxidized to $Co(DDC)_3$, which is very inert. It seems that this oxidation takes place in chloroform, but not in carbon tetrachloride.[81]

About 98% of the Mo remained in the organic phase with 12M HCl.

Selenium was not quantitatively backextracted; about 86% remained in the organic phase with 12M HCl. The inert character of $Se(DDC)_4$ and the extraction of the liberated Se(IV) as $SeCl_4$ by chloroform[93] may explain this behaviour.

Also tellurium was not quantitatively backextracted; about 3% remained in the organic phase with 12M HCl when the extraction and the backextraction were carried out in the dark, and about 25% when done in the normal laboratory light.

To demonstrate that DDC is completely destroyed by 12M HCl, 90 ml of water was added (to yield 1.2M HCl) into the separatory funnel after the 2 min shaking period and shaked again for 2 min. Arsenic, Cu, Hg and Sb remained ($\geqslant$99.8%) in the aqueous phase; these elements would be extracted ($\geqslant$99.5%) if the DDC were not destroyed (see Table 4). With the elements which are not quantitatively backextracted with 12M HCl, only the DDC not bound to the metal is destroyed.

Changes in the procedure may affect the results shown in Table 5. If the organic extract contains mg of the element (instead of 100 μg), then the beginning of the quantitative backextraction may be shifted to higher HCl concentrations; this effect can be overcome by increasing the shaking time ($>$2 min). With the standard procedure, times longer than 2 min may shift the "hole" between no backextraction and quantitative backextraction to the left.

Backextraction with bromine. Gold is not backextracted ($\leqslant$0.2); shaking for 10 min (instead of 30 s), waiting for 20 min (instead of 5 min) and using different aqueous phases to prepare the organic extract also resulted is no backextraction.

The excess of bromine goes preferentially into the organic phase and the fraction reduced to bromide goes into the aqueous phase.

If the aqueous extract after backextraction (5 ml) is diluted with 95 ml of water and extracted with Zn(DDC)$_2$ (2 min), Bi, Cd, Cu, Hg, In, Mo, and Te go into the organic phase ($\geqslant$99.5%). Arsenic and Sb are not extracted ($\leqslant$0.05%) because they have been oxidized to the (V) state. The acidity of the aqueous phase (pH about 1.5) hinders the extraction of Mn ($\leqslant$0.01%) and Co (0.7%).

Backextraction with HCl + H_2O_2. Antimony was only partially backextracted (5–10%). It was backextracted ($\geqslant$99.5%) when 9 ml of $\geqslant$1.7M NaOH was substituted for 9 ml of water. Probably a mixed complex Sb(V) – DDC – Cl is formed.

If the aqueous extract after backextraction (10 ml) is diluted with 90 ml of water and extracted by Zn(DDC)$_2$ (2 min), Bi, Cu, Hg, Pb, Se, and Te go into the organic phase ($\geqslant$99.5%). Arsenic is oxidized to As(V) and it is not extracted

5

($<$0.1%). With Sb, a mixture of Sb(III) and Sb(V) is obtained, from which only Sb(III) is extractable. Molybdenum is complexed more or less with the excess of H_2O_2, thereby the fraction extracted may vary greatly. The concentration of HCl in the aqueous phase (about 0.1M) hinders the extraction of some elements (Cd, 93% extracted; Co, 0.3%; In, 58%; Mn, $<$0.01%; Zn, $<$10%).

The reagents $M(DDC)_n$ [M = Bi, Cd, Co, Cr(III), Cu, Fe(III), Hg, In, MoO_2(II), Ni, Pb, Tl(I), Tl(III), Zn] are also completely destroyed by HCl + H_2O_2. This may be useful if the organic extract is prepared using a $M(DDC)_n$ other than $Zn(DDC)_2$ or HDDC. Because of the high stability of some of them, the general procedure calls for strong conditions. Proceed as follows. To a separatory funnel containing 60 ml of $1.7 \cdot 10^{-3}$M $M(DDC)_n$ in chloroform add 10 ml of 12.2M HCl and 0.20 ml of 30% H_2O_2. Shake several seconds by hand to mix, wait 5 min (keep the separatory funnel stopped to avoid losses of chlorine) and shake again for 2 min. Discard the organic phase. The aqueous phase contains now all the M as chloride.

<div align="center">*</div>

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