"MULTI-ELEMENT SOLVENT EXTRACTION IN ATOMIC ABSORPTION ANALYSIS"

by

N.J. Marshall

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ABSTRACT

PAPER PRESENTED TO THE FIFTH AUSTRALIAN SPECTROSCOPY CONFERENCE
IN PERTH ON JUNE 2ND, 1965.

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ABSTRACT

Routine analysis of geochemical materials (rocks, soils, waters, gossans) frequently requires the determination of traces of heavy metals in the presence of large amounts of foreign ions such as Fe^{3+}, Fe^{2+}, Mn, Ti, Ca, Mg, Na, K. Fusion methods of sample attack introduce large excesses of Na, K, or Li (depending on the flux used) into the system.

Atomic absorption analysis of the resulting aqueous sample solutions at very low metal concentration levels is limited by two factors.

1. Detection limits in the solid sample are at least ten times greater than the detection limits in solution. Thus for certain elements, e.g., Pb, Te, the detection limit is not low enough to enable precise analysis of certain materials.

2. Interferences due to high foreign ion content (Fe, Na, Ca etc.) can give apparent absorption readings which mask low level atomic absorption, particularly at wavelengths below about 2,400 Å. These are difficult to duplicate in standards when geochemical materials of widely differing and unknown composition are being analyzed.

Solvent extraction methods provide a means of concentration and simultaneous isolation of metal traces from solutions low in trace metal content and high in foreign ion content.

This paper gives the results of preliminary experiments in simultaneous extraction of several elements from "synthetic" rock and soil solutions.

Various solvents were investigated, and the ideal solvent must be:

1. lighter than water
2. quick to separate and clarify
3. not emulsify
4. immiscible with water
5. have a favourable partition coefficient for extraction of certain metal complexes.

The solvent must also be capable of direct aspiration into the flame without markedly altering flame characteristics and without the need to restrict the normal atomization rate.

Amyl acetate was best suited for this.

Various substituted dithiocarbamates were examined as chelating agents for the amyl acetate extraction of the heavy elements from sample solutions high in Fe, Mn, Ti, V, Ca, Mg, Al, Na, K.

The stability of non-aqueous standards is discussed and working curves are presented for the determination of Cu, Co, Ni and Pb in organic extracts.

The advantages and disadvantages of various substituted dithiocarbamates are discussed in their application to routine trace analysis.

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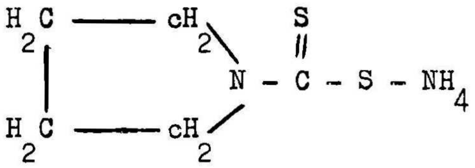
The advantages of solvent extraction in geochemical analysis, as well as the requirements of a solvent for atomic absorption work are outlined in the abstract, and will not be discussed further. Of a wide range of solvents investigated, amyl acetate was found to be the most suitable. The dithiocarbamates are well known for their property of forming highly insoluble coloured compounds with a number of elements of geochemical interest. This paper discusses the results obtained using NH_4 pyrrolidine dithiocarbamate, Na diethyl-dithiocarbamate and ~~Na succinimide dithiocarbamat~~e. Na Et xanthate

The pyrrolidine and succinimide dithiocarbamates were first described by Malissa and Schoffmann (1955) and pyrrolidine dithiocarbamate solvent extraction in biological analysis has been proposed by Allan, (1961) Willis (1962) and others.

Ferric iron is commonly a major constituent in geochemical samples, and interferes with the dithiocarbamate extractions unless removed or suppressed.

Ammonium Pyrrolidine Dithiocarbamate (APDC)



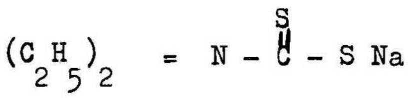
This reagent has been used for the estimation of traces of Pb by extraction of the complex into methyl isobutyl ketone at pH3. However its very low solubility in organic solvents restricts the application of this method to geochemical analyses.

A range of 19 solvents, irrespective of their flame behaviour, were tested for their solvent action on the Pb (APDC) complex, and none proved suitable.

Further, both ferric and ferrous iron interfere seriously and complexing reagents such as tartrate, citrate, oxalate and fluoride did not suppress iron interference with APDC at pH3.

Consequently, this reagent was abandoned for geochemical work, although it has been used with success by several workers for analysis of biological samples with a very low lead content and negligible iron content.

Sodium diethyldithiocarbamate (Na DDC)



$$(C_2H_5)_2 = N - \overset{S}{\overset{\|}{C}} - S\,Na$$

The Pb complex forms in both acid and alkaline solutions. However, the diethyldithiocarbamate ion is not stable in acid solution, so it is desirable to work with alkaline media.

Iron also reacts with diethyldithiocarbamate making the co-extraction of trace elements unreliable. Tartrate, fluoride, acetate, cyanide and citrate were tested as masking agents and it was found that a large excess of citrate would inhibit the formation of Fe DDC in alkaline solution, but does not altogether prevent it. Citrate is also necessary to prevent precipitation of metal hydroxides.

Thus trace amounts of Pb^{++} in the presence of a large excess of iron can be extracted into amyl acetate from ammoniacal citrate solution. Some Fe DDC complex forms and is co-extracted to give a brown solvent phase, but atomic absorption blank tests show that light scattering from this small amount of iron when introduced into the flame is negligible.

In the high concentration solutions used in geochemical work, non-atomic absorption is often important. Alkali and alkaline earth elements are not extracted - hence freedom from this error.

A two-stage extraction of 1000 γ Pb^{++} into 10ml amyl acetate showed that a single extraction for 2 minutes is virtually complete.

Similar experiments have shown that copper is readily extracted along with lead from ammoniacal citrate solutions. In this case, copper extraction was calculated at 99.2% at the first stage.

For atomic absorption methods, it is essential to run a calibration curve with each batch of analyses, and to avoid the necessity for solvent extraction from aqueous standards each time, it is more convenient to have on hand stocks of metal diethyldithiocarbamate standards in amyl acetate. The stability of these organic standards was assessed by comparing freshly prepared organic extracts with stored ones.

It was found that standards stored on the shelf are not very stable, and over a period of 12 days, copper and lead diethyldithiocarbamates in amyl acetate suffered serious loss in strength.

Comparative tests on refrigerated standards compared with fresh standard extracts showed that refrigerated standards are stable for several days.

Table 1 compares percent transmission for fresh standards of cobalt and nickel with 4-day-old refrigerated standards.

TABLE 1

ppm in solvent	Co organic standards % transmission		Ni organic standards % transmission	
	Fresh	4 day-old	Fresh	4 day-old
1	87.2	86.8	87.5	86.8
2	74.4	76.0	72.0	71.5
4	54.6	54.0	50.2	50.2
6	44.0	43.2	35.3	35.0
8	35.4	35.2	25.3	25.5
10	29.0	25.0	19.0	19.0

The simultaneous extraction of traces of Cu, Co, Ni, and Pb in the presence of large amounts of interfering ions normally encountered in geochemical sample solutions was attempted next.

An ammoniacal citrate stock solution of the following composition was prepared free from Cu, Co, Ni and Pb: Fe^{3+} = 5,000 ppm, Al = 1000 ppm, Mn = 1,000 ppm, Ca = 500 ppm, Mg = 500 ppm.

20 ml of the above solution was added to a series of aqueous standards each containing Cu, Co, Ni and Pb, followed by, 5 ml of ½% sodium diethyldithiocarbamate and water to 100 ml. These standards were extracted with 10 ml of amyl acetate by shaking for 2 minutes, and the Cu, Co, Ni and Pb in the solvent phase determined by atomic absorption technique.

Under these conditions,0.05 millimoles of the diethyldithiocarbamate complexing metals (Cu, Ni etc) can be extracted. Higher reagent concentrations will enable extraction of correspondingly larger amounts of metal up to the solubility limit of the complex in the organic phase (this is about 300 ppm for Pb).

Table II shows the concentration ranges covered and percent transmissions obtained.

TABLE II

percent transmission		ppm in aqueous soln.	final ppm in amyl acetate
		LEAD	
100		0	0
82.0		0.5	5
66.5		1	10
44.0		2	20
30.3		3	30
22.0		4	40
17.2		5	50
		COPPER	
96.8		0	0
83.5		0.05	0.5
75.2		.10	1
56.8		.20	2
41.2		.30	3
35.0		.40	4
28.0		.50	5
		COBALT AND NICKEL	
Co	Ni		
99.2	98.8	0	0
90.0	82.0	.1	1
82.3	66.9	.2	2
65.4	45.2	.4	4
53.5	31.0	.6	6
45.5	22.0	.8	8
42.0	17.2	1.0	10

All in the presence of:

1,000 ppm Fe^{3+}
200 ppm Al
200 ppm Mn
100 ppm Ca
100 ppm Mg
.15 N Cl^-
4% triammonium citrate solution.
$SO_4^=$, $NO_3^=$ from added salts.
NH_4OH

Figure 1 illustrates the type of calibration curve obtained for nickel, using the percent transmission data relating to Table II.

For comparison, the corresponding calibration curve for pure aqueous nickel solutions is shown. This calibration graph for organic extracts is similar to those obtained for copper, lead, and cobalt extracted from pure aqueous solutions and to copper and lead extracted from the aqueous solutions rich in competing ions.

Note, however, that the organic calibration graph for cobalt in the presence of competing ions is greatly divergent to that for cobalt extracted in the absence of competing ions.

It would appear that the competing cations, (probably iron), have stability constants with diethyldithiocarbamate which are comparable with the stability constants of cobalt diethyldithiocarbamate so that in the presence of a large excess of iron, formation of the cobalt complex is suppressed. This is not evident with the other elements examined.

To accurately assess the influence of the competing ions on the Cu, Pb, Co, Ni diethyldithiocarbamate system, a high and a low standard of a mixture of these metals was extracted both in the presence and absence of competing ions. Corresponding blanks were run both on the pure ammoniacal citrate solution and on the same solution in the presence of competing ions.

Table III illustrates the method and results.

TABLE III

A1 = .05 ppm Cu, .10 ppm Co and Ni, .50 ppm Pb is ammoniacal citrate solution.

A2 = .4 ppm Cu, .8 ppm Co and Ni, 4 ppm Pb in ammoniacal citrate solution.

B1 = Concentrations as for A1, but competing ions present (i.e. 1,000 ppm Fe^{3+}, 200 ppm Al, 200 ppm Mn, 100 ppm Ca, 100 ppm Mg, .15N Cl^-, in ammoniacal citrate solution.

B2 = Concentrations as for A2, but above competing ions present.

N.B. All readings have been corrected for blanks.

SAMPLE	AAS readings as % transmission for amyl acetate extracts of 10X aqueous soln. strength.			
	Cu	Pb	Ni	Co
A1	87.0	80.3	81.5	86.0
A2	37.1	18.7	22.9	28.5
B1	86.3	79.8	80.5	92.3
B2	37.9	19.0	24.8	43.8

Thus Cu, Pb, Ni can be determined in iron rich geochemical samples using diethyldithiocarbamate/amyl acetate extracts from ammoniacal citrate solutions, whereas Co can only be determined in reasonably "pure" solutions.

Stability tests similar to those previously described on standard organic extracts show that:

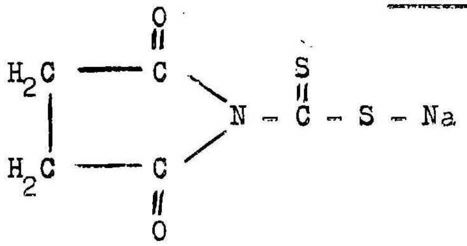
1. Co, Ni, Cu and Pb standards are stable under refrigeration for 10 days, but show slight loss of strength after 15 days.

2. Standards prepared from iron rich solutions are discolored brown due to some iron being co-extracted as the complex, despite the presence of citrate. However these "unknowns" containing iron impurity are stable with respect to Cu, Pb, Co, Ni content for at least 24 hours.

Therefore the use of diethyldithiocarbamate and solvent extraction from ammoniacal citrate can be used as a rapid routine procedure, as "unknowns" in the presence of iron are stable enough for analytical application and can be compared with AAS calibration curves prepared from stored, refrigerated standards made up weekly.

Sodium Ethyl Xanthate NaEX

~~Sodium Succinimide Dithiocarbamate~~ (~~Na S2C~~)



As with the other dithiocarbamates this reagent reacts with most metals excepting alkali's and alkaline earths. However it has several important advantages which are:

1. it does not react with ferrous iron.

2. it reacts quantitatively with Se and Te.

3. (it is fairly stable in acidic solutions.) Not so

Unlike diethyldithiocarbamate, the NaEX ~~succinimide~~ derivative does not react with many elements above pH8, although cobalt reacts up to pH14.

Most of the metal complexes in acidic solution are readily soluble in amyl acetate, but the Cu and Pb complexes have a low saturation limit - about 3 ppm in the organic phase for Cu.

The cobalt NaEX ~~succinimide dithiocarbamate~~-amyl acetate reaction was investigated by comparing atomic absorption readings for identical standards complexed and extracted at various pH's.

It was found that optimum extraction occurred in the pH range 2.5 - 4.

Figure 2 shows the calibration curve obtained for the extraction of cobalt standards with this reagent. The presence of 1,000 ppm Fe, 200 ppm Al, 200 ppm Mn, 100 ppm Ca and 100 ppm Mg plus 4% triammonium citrate and 0.15N Cl^- at pH3 had little effect on the cobalt extraction.

The cobalt extract was not discolored by the Fe^{3++} complex, as was the case with diethyldithiocarbamate at pH 8-9, but after correcting for different blanks as in Table III, it was found that a 1 ppm cobalt extract from pure 0.1 ppm aqueous solution gave a transmission reading of 83%, while an identical extract from .1 ppm Co aqueous solution in the presence of competing ions (1,000 ppm Fe^{3++} etc) gave a reading of 85%.

This lowering in sensitivity by 2% is not due to any Fe interference, as it was subsequently found in connection with tellurium analysis that the high salt strength due to the 4% ammonium citrate present has slightly lowered the distribution coefficient of the cobalt complex between the aqueous and organic phases.

Tests on the stability of stored cobalt succinimide dithiocarbamate standards in amyl acetate showed that refrigerated standards are stable for about a week, and thereafter show a loss in strength of 18% over 6 weeks.

It is emphasized that this situation is the worst likely to be encountered in practice, as the reagent was of doubtful purity.

Thus the use of ~~sodium succinimide dithiocarbamate~~ added to an aqueous citrate solution at pH3 in the presence of large excesses of competing ions, followed by subsequent amyl acetate extraction for 2 minutes, is a valid method for the rapid routine analysis of small traces of cobalt in geochemical samples of unknown matrix composition.

Finally, experiments were done on the solvent extraction of tellurium from geochemical sample solutions. Tellurium is of interest in geochemical work but no really satisfactory method of rapid analysis at the trace element level is available.

The detection limit for tellurium in aqueous solutions is only 1 ppm for 2 percent absorption (using Techtron equipment) - readings below 2% absorption are unreliable due to lamp instability. This means an effective 50 ppm detection limit in the solid as a high dilution factor must be used to suppress light scattering at the 2143Å wavelength by salts introduced into the flame.

It is therefore necessary to use a solvent extraction procedure whereby tellurium can be simultaneously concentrated and separated from anions and the matrix cations.

Tellurium complexes readily with sodium succinimide dithiocarbamate in acid solution, and the resultant precipitate is readily soluble in amyl acetate.

It was established that tellurium extraction is quantitative at least in the acid range $\frac{1}{4}$ to 5% HCl, but is not quantitative above pH1-2.

Citrate is not dissociated sufficiently at such low pH values to effectively complex excess ferric iron and prevent its reaction with succinimide dithiocarbamate, while ferrous iron, which does not complex, cannot be tolerated in tellurium solutions, (these are readily reduced to colloidal Te). Orthophosphoric acid, however, has a much lower pK than citric and in dilute acid effectively suppresses the formation of the Fe^{3+} dithiocarbamate complex.

Sulphuric acid up to at least 10%, phosphoric acid to at least 3% and competing ions have no influence on tellurium extraction, as identical atomic absorption readings were obtained for the extraction of 20 Te from 100 ml of pure 10% H_2SO_4 and from 100 ml of a solution containing 3% HCl, 3% phosphoric acid, 2,000 ppm Fe^{3+}, 200 ppm Ca, 200 ppm Mg, 400 ppm Al, 400 ppm Mn.

The distribution coefficient is high enough to give virtually complete extraction at the 1st stage, since almost identical absorption readings were obtained for the extraction of 20 γTe from 10 ml of solution as from 200 ml of solution.

Thus it has been proved possible to quantitatively extract trace quantities of tellurium from a synthetic sample solution containing a 10,000 fold excess of iron as well as other elements, provided about 3% phosphoric acid is present to suppress iron interference. The organic solvent is free of interfering elements.

Figure 2 illustrates the calibration curve obtained for tellurium complex in amyl acetate.

The blank reading of 6% absorption at 2143 Å is entirely due to the presence of the reagent in the solvent phase.

Assuming a detection limit of 2% absorption for Te, then 0.8 ppm Te in the organic phase can be detected.

Since about 3 ml of solvent is required for aspiration, the amount of tellurium required for analysis is 2.4 γ Te.

This can be extracted from 100 ml of aqueous solution of .024 ppm Te content, so if 10 grams of rock is digested and made up to 100 ml of solution, the detection limit is 0.24 ppm Te in the rock.

Even better detection limits are possible when more stable Te lamps become available, as then readings of the order of 1% absorption can be read by scale expansion.

Another technique of further increasing sensitivity in all this work is to prepare larger volumes of amyl acetate extracts while maintaining the same optimum solid/solution/solvent ratio, then evaporating down the volatile solvent phase under reduced pressure to say 1/5 or 1/10 its original volume.

Using these complexing and solvent extraction techniques, a 5g sample can be dissolved in 100 ml of solution and the trace elements extracted into as little as 3 ml of amyl acetate (sufficient to give two readings). The subsequent extracts are free of salts and absorption readings as low as 1% (for Cu, Pb, Ni, Co) may be regarded as reliable. If solvent extraction is not used, a dilution factor of 50 is incurred where the sample is completely dissolved, as only about 2 percent of mixed salts in aqueous solution can be tolerated in the flame. Even then there can be significant light scattering due to salts in the flame, and a 1% absorption figure could not be regarded as reliable.

Table 4 shows the detection limits which can be attained in practice, using the techniques described, without solvent evaporation.

Table IV - Detection limits at 1% absorption

	Solvent extraction procedure			Straight aqueous solution	
Element	ppm in organic soln.	equivalent ppm in aqueous phase	ppm in solid	ppm in aqueous soln.	ppm in solid
Pb	.25	.008	.15	0.4	20
Cu	0.04	.0012	.024	0.06	3
Ni	.05	.0015	.03	.08	4
Co	.05	.0015	.03	.08	4

Sample digestion techniques such as dilute acid extraction can improve the sample/solution ratio and hence the detection limits in straight aqueous solutions. In these cases, detection limits in organic extracts are correspondingly improved, and this table is intended as a guide only.

Addendum

During the subsequent discussion, Dr. David pointed out that he had experienced fluctuating readings with volatile organic solvents due to solvent vapour absorbing in the light path of the instrument. This problem was not encountered in this work, possibly due to the fact that the whole equipment was mounted in a laboratory fume hood.

Dr. Willis asked whether solvent extraction methods had been used for tin analysis, as well as for other metals besides Cu, Pb, Co and Ni. At this stage the proposed methods had not been sufficiently tested for other elements as the work is still in its early stages, and suitable apparatus for tin work was not to hand. It is intended to expand the scope of this paper to include about a dozen geochemically important elements.

In subsequent personal communications, Mr. J.E. Allan and Mr. Walter Slavin suggested that the use of isobutyl methyl ketone solvent instead of amyl acetate would give enhancement factors due to greater solvent atomization efficiency of 3 to 4 compared with the enhancement factor of 1.5 to 2 found for amyl acetate compared with aqueous solutions. Methyl isobutyl ketone was not used in this work as it was found that a luminous smoky flame resulted with the equipment used and that when this flame was brought "back to normal" by reducing acetylene flow rate only there was insufficient fuel to support combustion on removal of the ketone with the result that the flame blew out. At their suggestion the luminous ketone flame was adjusted by increasing the air flow as well as reducing acetylene flow (to a higher flow rate than previously). Under these conditions a normal blue flame resulted which did not "lift" on removal of the ketone.

It is probable, therefore, that the use of methyl isobutyl ketone instead of amyl acetate in the techniques described will result in steeper calibration graphs and improvement in sensitivity by a factor of approximately two. It should be noted, however, that a solution/solvent ratio of 33 1/3 as suggested for amyl acetate (solubility 0.18%) would not be applicable with the ketone (solubility 1.9%) unless the aqueous phase has been initially equilibrated.

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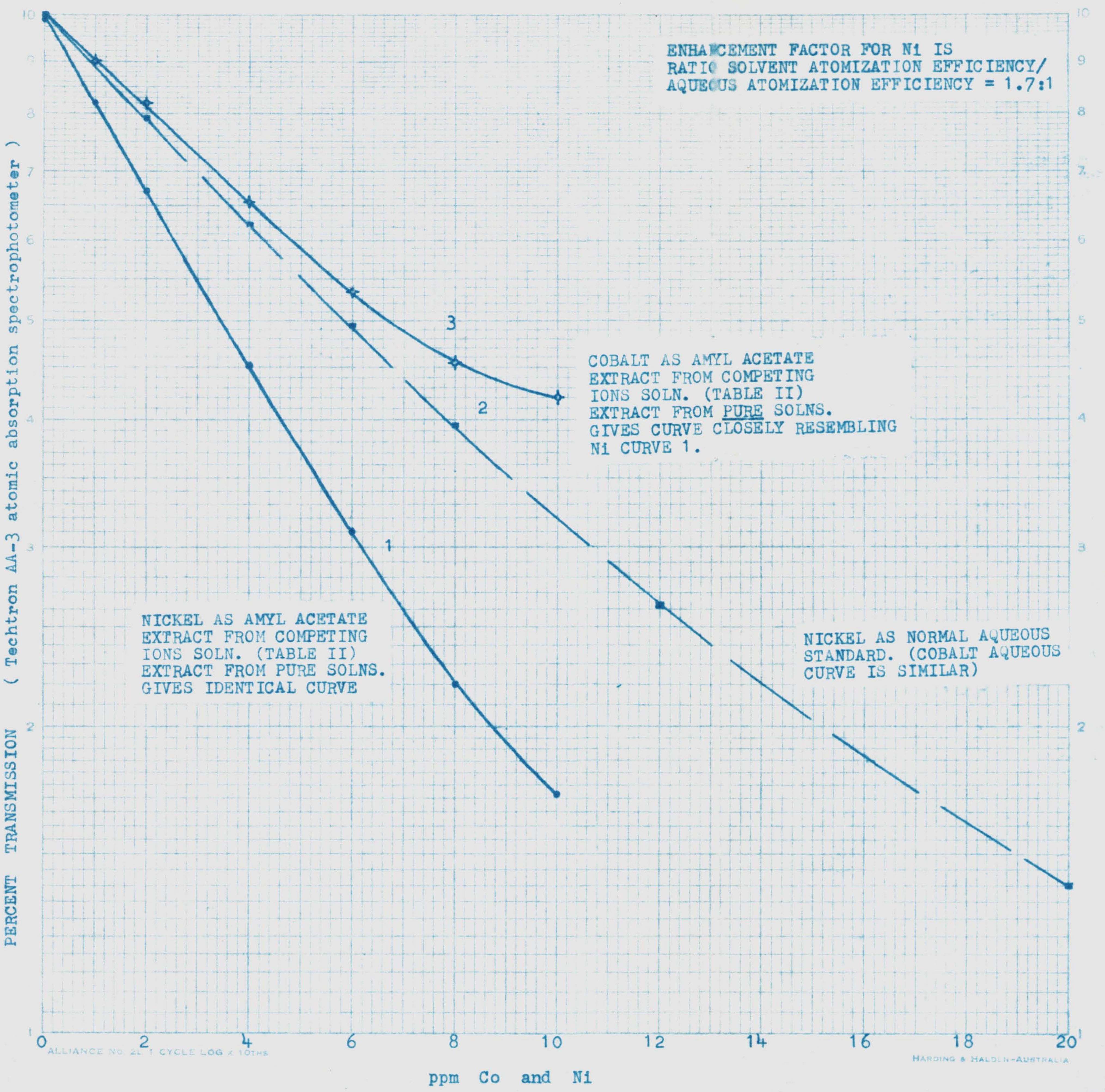
FIGURE I

COMPARATIVE CALIBRATION CURVES (Using diethyldithiocarbamate)



ENHANCEMENT FACTOR FOR Ni IS
RATIO SOLVENT ATOMIZATION EFFICIENCY/
AQUEOUS ATOMIZATION EFFICIENCY = 1.7:1

COBALT AS AMYL ACETATE
EXTRACT FROM COMPETING
IONS SOLN. (TABLE II)
EXTRACT FROM PURE SOLNS.
GIVES CURVE CLOSELY RESEMBLING
Ni CURVE 1.

NICKEL AS AMYL ACETATE
EXTRACT FROM COMPETING
IONS SOLN. (TABLE II)
EXTRACT FROM PURE SOLNS.
GIVES IDENTICAL CURVE

NICKEL AS NORMAL AQUEOUS
STANDARD. (COBALT AQUEOUS
CURVE IS SIMILAR)

FIGURE II

COBALT and TELLURIUM CALIBRATION CURVES

(Using succinimide dithiocarbamate)