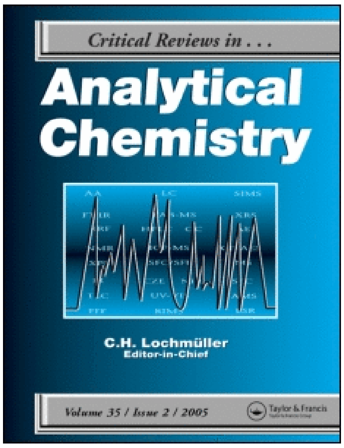
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

The Analytical Applications of Dithizone

H. M. N. H. Irving; Georg Iwantscheff

To cite this Article Irving, H. M. N. H. and Iwantscheff, Georg(1980) 'The Analytical Applications of Dithizone', Critical Reviews in Analytical Chemistry, 8: 4, 321 — 366

To link to this Article: DOI: 10.1080/10408348008542714

URL: http://dx.doi.org/10.1080/10408348008542714

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE ANALYTICAL APPLICATIONS OF DITHIZONE

Author: H. M. N. H. Irving
Department of Analytical Science
University of Cape Town
Cape Town, South Africa

Referee: Georg Iwantscheff
Nürnberg-Laufamolz, West Germany

TABLE OF CONTENTS

I. Introduction

II. Basic Properties of Dithizone
  A. Preparation and Structure
  B. Tautomerism in Solution
  C. The Solubility of Dithizone in Aqueous and Organic Solvents
  D. Deterioration of the Reagent and its Solutions

III. Metal Dithizonates and Liquid-Liquid Extraction
  A. Metal-dithizone Complexes
  B. Basic Principles of Dithizone Extractions
  C. Spectrophotometric Finishes
    1. Monocolor Method
    2. Mixed Color Method
    3. Reversion Method
  D. Other Separation Processes
    1. Thin Layer Chromatography (TLC)
    2. Column Chromatography

IV. A Survey of Recent Literature
  A. Antimony
  B. Arsenic
  C. Bismuth
  D. Cadmium
  E. Cobalt
  F. Copper
  G. Gallium
  H. Gold
  I. Indium
  J. Iron
  K. Lead
  L. Manganese
  M. Mercury
  N. Nickel
  O. Palladium
  P. Platinum

- Q. Polonium
- R. Selenium
- S. Silver
- T. Tellurium
- U. Thallium
- V. Thorium
- W. Tin
- X. Uranium
- Y. Zinc

V. Dithizone and Electrochemistry
- A. Basic Studies
- B. Applications
  - 1. Polarographic Finishes
  - 2. Amperometric Analysis
  - 3. Stripping Voltammetry
  - 4. Coulometric Titrimetry

VI. Some Special Applications of Dithizone
- A. Preconcentration
- B. Atomic Absorption Spectrophotometry
- C. Activation Analysis and Substoichiometry
- D. Ion-selective Electrodes
  - 1. General Theory
  - 2. Applications
- E. Additional Applications
  - 1. Quantitative Tests
  - 2. Ligand and Metal Exchange
  - 3. Titrimetry
  - 4. Kinetic Effects
  - 5. Concluding Remarks

References

I. INTRODUCTION

The analytical reagent dithizone has now been used in analytical chemistry for just over 50 years, and forms the subject of an extensive literature comprising well over 2200 papers. Research work on this reagent was first carried out by Hellmuth Fischer, originally as a purely personal interest — virtually a hobby. However, the Siemens organization at Erlangen, Germany, was fortunate indeed to be able to employ his expertise when they were faced with the problems of determining small amounts of metallic impurities in certain highly purified metals.[1,2] In this field, its great sensitivity and considerable selectivity made an immediate impact. The intense color of the reagent itself — and that of each of its metal complexes, their sparing solubility in water, but considerable solubility in organic solvents — led Hellmuth Fischer, and later many others, to elaborate liquid-liquid extraction procedures for concentrating and separating desired metals and to devise a whole variety of absorptiometric finishes. Selectivity was enhanced by a careful control of the pH employed in extractions, and by the use of masking agents.

The use of dithizone soon spread to other fields: initially for the determination of lead in a variety of organic and pharmaceutical materials, in agricultural and biochemical samples, and notably in forensic investigations. Dithizone proved invaluable for the determination of lead and other elements such as zinc, silver, copper, cadmium, thallium, and bismuth, etc., in the analysis of rocks and minerals, natural waters and effluents, and every conceivable kind of natural and industrial product. A special impetus in the late 1940s came from the growing availability of absorptiometers (filter photometers) and spectrophotometers which, while displacing the cruder earlier colorimetric procedures by measurements with a narrow band of wavelengths, enormously increased the precision of measurements, particularly those involving multicomponent systems.[3] By 1960 the techniques for analytical determinations using dithizone were well established, and the decade 1955 to 1965 was responsible for nearly half the publications dealing with the uses of this reagent in trace analysis: for besides reports of detailed procedures for the determination of the "dithizone metals" Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn, Pt, Au, Hg, Tl, Pb, and Bi, methods had been discovered for the determination of organometallic cations such as RHg^+ and $ArHg^+$,[4,5] R_2Sn^{2+} and R_3Sn^+,[6,7] R_3Pb^+ and R_2Pb^{2+},[7] and R_2Tl^+ and Ar_2Tl^+.[7] The use of metal dithizonates in chromatographic separations was being increasingly developed, and the strictly integral stoichiometry of these metal-ligand complexes combined with the advantages of liquid-liquid extraction led Růžička and Starý to introduce them in the powerful new technique of substoichiometry, which has proved such a valuable procedure in neutron activation analysis.[8-11]

The high partition coefficients favoring the organic phase that had proved so useful in trace metal determinations as a preliminary to an absorptiometric finish, could equally well be employed to preconcentrate and separate the dithizone metals in a variety of procedures in which many different physical methods of analysis, e.g., X-ray fluorescence, atomic absorption, or fluorescence spectroscopy, cathodic stripping, and voltammetry etc., were used as finishes. Conversely dithizone could be used as a selective "scavenger", and in conjunction with other reagents such as diethylhexylphosphoric acid, 8-quinolinol, or tributylphosphate provided a powerful tool for stripping and concentrating trace metals in many environmental analyses.

The number of publications dealing with dithizone reached its peak during the period 1960 to 1965. The subsequent fall off can scarcely be explained by the fact that by then detailed procedures had been worked out for the determination of dithizone metals in almost every conceivable type of material,[12] though occasional papers still report the application of the old well-proven absorptiometric procedures to new varieties of samples, e.g., the determination of mercury in acidic brine electrolytes,[13] or the determination of silver impurities in some thermoelectric materials,[14] or thin semiconductor layers.[15] The real explanation seems rather to be the rapidly growing popularity of atomic absorption spectroscopy (AAS) and the widespread availability of many suitable and not too costly instruments. Here the sensitivity of the technique and its adaptability to so many different elements combined with the comparative ease of preparing samples for nebulization (and indeed the feasibility of flameless excitation) provides obvious advantages for routine analyses. For there is no doubt that the extreme sensitivity of dithizone to traces of metals imposes special practical problems connected with the cleanliness of all glassware, the purity of reagents used, and provision for better-than-average working conditions if high blanks and spurious results are to be avoided; moreover in quantitative procedures, a higher standard of manipulative skill is required in dithizone procedures that are inherently slower though, with some lack of precision, they could be adapted to automated analysis.

Despite this change of emphasis in the quantitative finish, dithizone continues to find new uses in other analytical fields such as a foam supported reagent for column chromatographic separations or for metal indicating columns,[16] and metal dithizonates play a specially useful role in certain ion-selective electrodes.[17]

Rather than cover well-trodden ground and elaborate on the (by now) classical procedures for determining individual metals that have been described and reviewed in many books,[18-23] and treated in great detail in Iwantscheff's authoritative book *Das Dithizone und seine Anwendung in der Mikro- und Spurenanalyse,*[12] with its fully detailed bibliography covering the years 1878 to 1969 and partial coverage to the middle of 1971, we shall concentrate on work published in the last decade. However, to set the scene it will be appropriate to review some of the basic properties of dithizone and its metal complexes, their behavior in liquid-liquid extractions, and the various ways in which quantitative determinations can be carried out by visual colorimetry or absorptiometry. The theory of these processes is of considerable relevance to any intelligent planning of separations; fortunately, it has been studied in some depth. Indeed the more academic aspects of the chemistry of dithizone has attracted a good deal of attention and is reviewed in a recent monograph.[3]

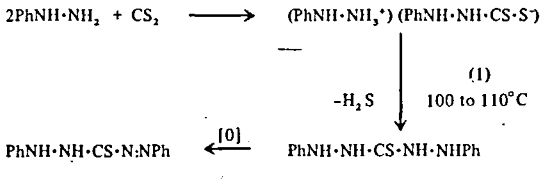
After analyzing a typical extraction-spectrophotometric procedure, we shall proceed to illustrate the dithizone method for the determination of a number of metals and organometallic cations, paying special attention to those where points of uncertainty or contention still exist, and conclude with a summary of the many other analytical applications of this versatile reagent in as logical an order as possible, while emphasizing those fields where there has been the most interesting or promising developments in recent years.

At least a hundred analogues of dithizone have been prepared starting with the synthesis of 1,5-di(2-naphthyl)thiocarbazone by Suprunovitsch in 1938. Several scores of analogues prepared by Pupko and Pel'kis and other Russian workers would seem to have been insufficiently purified judging from data published by Freiser, Irving, Kiwan, Ramakrishna, Takei and Kato, and co-workers. Although certain claims of enhanced metal complexing stability or improved spectral characteristics or other advantages have been made from time to time,[24] it remains true that after 50 years of international usage the original reagent shows no sign of being supplanted. For example, where substitution in the phenyl rings has led to an increase in the molar absorption coefficient, ε, the partition equilibrium has almost invariably been shifted to less convenient and higher pH ranges. Notwithstanding any drawbacks, it is easy to endorse Iwantscheff's summing up "So ist das alte einfache Dithizon der Renner in der exakten Spurenanalytik geblieben".[2]

II. BASIC PROPERTIES OF DITHIZONE

A. Preparation and Structure

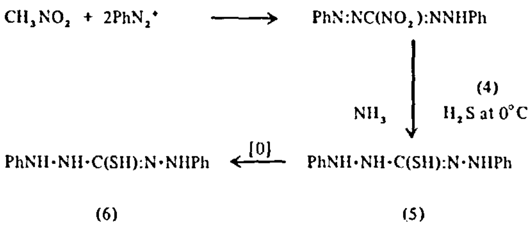
Dithizone is the trivial name given to a substance first prepared by Emil Fischer in 1878 by the following route:[25]



(3) (2)

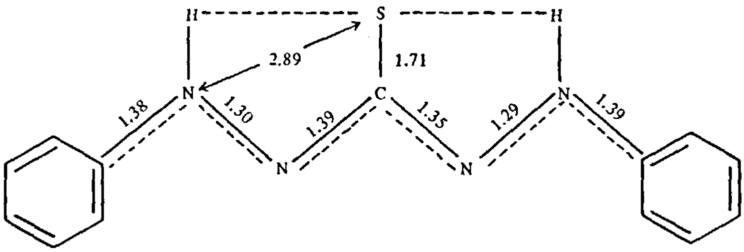
The crystalline compound, formulated as $(C_{13}H_{12}N_4S)_2$, ZnO was analyzed and "salts" with lead (red), silver (brown-violet), and mercury (I) and (II) (red-brown), were also prepared. They were all soluble in chloroform, but insoluble in water.

Forty-eight years later the same compound was prepared by Bamberger et al. starting from nitromethane and a diazonium salt:[26]



The formulation as a thioketone (3) led to the name diphenylthiocarbazone (whence dithizone), whereas the formulation (6) as a thiol is responsible for the names *N,N'*-diphenylformazylmercaptan, *N,N'*-diphenyl-C-mercaptoformazan, 3-mercapto-1,5-diphenylformazan and 1,5-diphenyl-3-thiolformazan. It is listed in *Chemical Abstracts* under the systematic name diazenecarbothioic acid, phenyl-, 2-phenylhydrazide, and until recently under phenylazothioformic acid 2-phenylhydrazide.

When pure, dithizone of composition $C_{13}H_{12}N_4S$ (M_r = 256.3) forms a violet-black crystalline powder of density 1.35×10^3 kg m,$^{-2}$ which melts with decomposition at about 169°C. In the solid state the molecule (7) is nearly planar with the C-S bond lying on the intersection of two mirror planes, although the two phenyl groups are slightly twisted out of the mean plane and in opposite directions.[27]

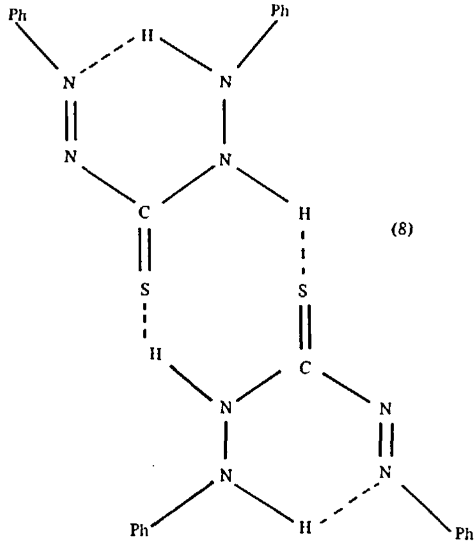


(7)

The π-electrons in the chain N-N-C-N-N are delocalized and the sulfur atom is symmetrically hydrogen bonded.

B. Tautomerism in Solution

Dithizone dissolves readily in aqueous alkali and behaves as a typical thiol in forming insoluble compounds with mercury and other heavy metals, and in its ease of oxidation. On the other hand, Fischer's synthesis favors a thioketone structure (3). Since spectra in the visible region of solutions in organic solvents exhibit two well defined bands at about 420 and 620 nm (Figure 1), it was assumed quite early that the two tautomers coexisted in solution, the thiol form (5) being responsible for the band at the lower wavelength. This point of view is not universally accepted and in Carlin's doctoral thesis it was concluded that solutions of dithizone in organic solvents comprise a thione-thione dimer (8) and a thiol-form with extensive hydrogen bonding, which had the structure (7), later established for the solid reagent itself.[28]



(8)

This work, which has unfortunately not been reported in the open literature, ascribes the *lower* wavelength band to the thione-form, λ_{max} 450 nm; there is moreover no evidence for association in solution to support Carlin's views. The reflectance spectrum (Figure 1) shows one clearly defined band at about 450 nm corresponding to the (thioketone) form found in solution; there is only a shoulder covering the region 550 to 580 nm, suggesting that the thioketone predominates in the solid state.[29]

Coleman et al. would not agree with these conclusions.[30] Although they were aware that the relative intensities and values of λ_{max} for the two bands in the visible spectrum of dithizone varied with the solvent (for example in chloroform $\lambda_{max,1}$ = 605 nm (ε = 4140 m^2 mol^{-1}) and $\lambda_{max,2}$ = 440 nm (ε = 1590) whereas in n-hexane the corresponding values are $\lambda_{max,1}$ = 617 nm (ε = 2760) and $\lambda_{max,2}$ = 447 nm (ε = 2540),[3] they were unable to interpret them rigorously "since they appear to be complicated by acid-base equilibria, trace metal effects, and even oxidative decomposition of the dithizone." These last comments are quite unjustified for the spectrum of pure dithizone is absolutely reproducible in any solvent provided the reagent and the solvent are rigorously purified and any glassware used specially cleansed. Indeed the ratio of $\varepsilon_{max,1}/\varepsilon_{max,2}$, the so-called peak ratio is probably the most sensitive index of reagent purity.

Although dithizone was too insoluble for them to measure its nmr spectrum, they succeeded with the soluble analogue 1,5-di(*o*-ethylphenyl)thiocarbazone and in $CDCl_3$ solution found 6 methyl protons at τ = 8.6, 4 methylene protons at τ = 2.0, 8 aromatic protons at τ = 1.9 and 2.67, and 1.6 protons at τ = −2.03. The signal at τ = −2.03 showed no evidence of splitting over the range +50 to −45°C in $CHCl_3$ (in fact it sharpened at lower temperatures) and disappeared on adding CH_3OD. They interpret these results as indicating a single (equivalent) structure (7) (as subsequently found for solid dithizone), rather than rapid exchange between a form containing SH and a form containing NH.

It is important to notice that Coleman et al. only report a total of 19.6 protons, and more significantly only 1.6 instead of the 2.0 nonaromatic protons. More recent work at Leeds with an instrument of higher resolving power has provided the NMR spectrum of dithizone itself in $CDCl_3$: two signals at τ = −2.61 and τ = 9.03 of integrated area 3:1 completely account for the two nonaromatic protons.[29] The peak at τ = 9.03 occurs in the characteristic region for an SH band in the absence of significant hydrogen

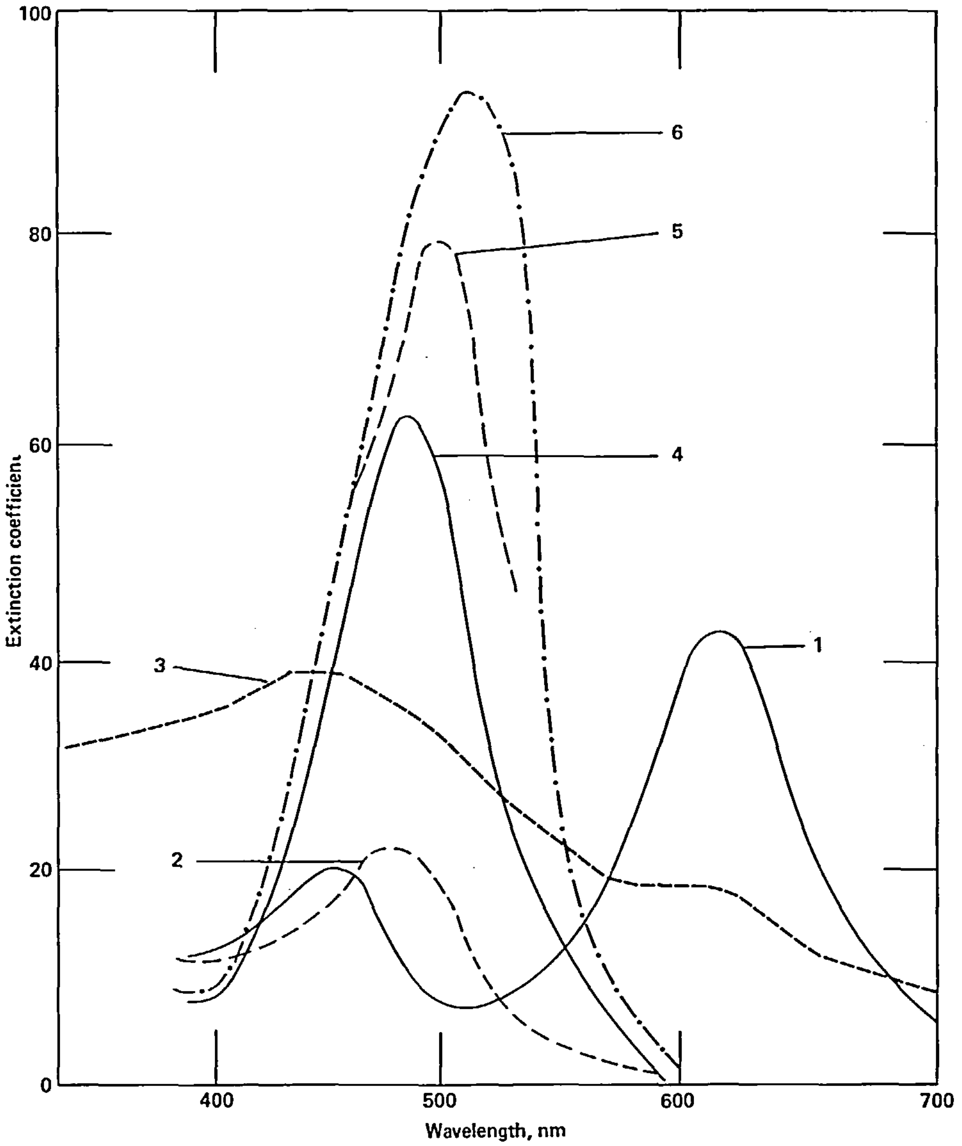
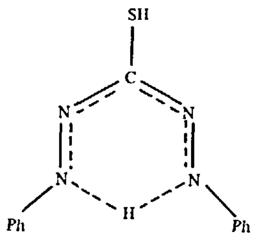
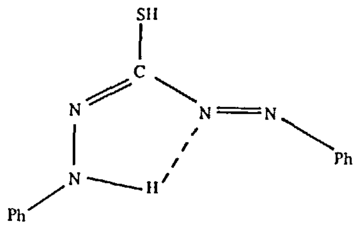


FIGURE 1. The absorption spectra of solutions in CCl_4 of (1) dithizone, (4) mercury(II) dithizonate, (5) bismuth dithizonate, (6) zinc dithizonate; (2) is the absorption spectrum of the anion, HDz^-, in water; (3) the reflectance spectrum of dithizone (not to scale).

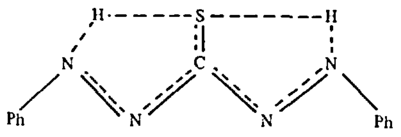
bonding, which ties up with the corresponding interpretation of the infrared peak at 2590 $cm.^{-1}$ The absence of absorption in the infrared region 3100 to 3500 cm^{-1} points to the absence of a free :NH group and indicates that any :NH present must be very strongly hydrogen bonded. Extensive measurements on analogues of dithizone and on both of the tantomeric forms of *S*-methyldithizone can best be interpreted if solutions of dithizone do contain more than one form in tautomeric or conformational equilibrium, and these could be an internally hydrogen-bonded 1,5-diphenyl-3-mercaptoformazan (9) or less probably (10) comprising 25% of the whole in $CDCl_3$, and a thione form that could be (7)



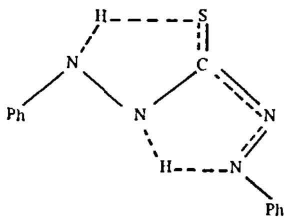
(9)



(10)



(7)



(11)

or (11). Pel'kis and Dubenko have certainly accepted the hypothesis that solutions of dithizones contain two forms in equilibrium, and have sought to calculate the percentage of each in terms of their extinction coefficients and from the spectrophotometric properties of the corresponding *S*-methyl derivatives that one might hope would lock the tantomerism exclusively in the thiol form. Unfortunately the *S*-methyl derivatives themselves exhibit cis-trans tantomerism about an·N=N· bond, and failure to take this into account or to justify other postulates has led the Russian authors to argue *in circulo probando,* though it does not seem profitable to enter into detailed discussion here.[3]

The final protagonists to enter the lists have approached the problem by calculating the energies and intensities of electron transitions of different forms of dithizone by molecular orbital theory (LCAO MO SCF LCI) and comparing calculated oscillator strengths at many wavelengths with experimentally determined spectra.[31] Considerable success attended their calculation for the protonated species of dithizone, H_3Dz^+, in 60% H_2SO_4 and their calculations for the anion HDz^- and the possible anion Dz^{2-} seem not unreasonable.

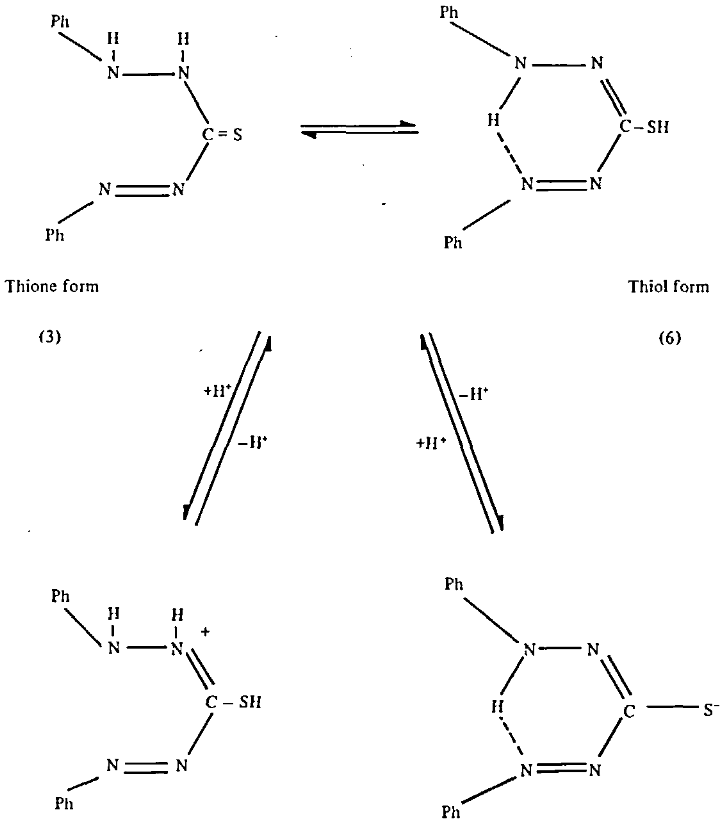
Their calculation for dithizone itself is based on structure (7), and predicts two strong bands of comparable intensity, B at about 440 (which corresponds to the experimental peak at 452 nm) and the other, D, at about 280 nm (which does not agree with any feature of the experimental absorption curve). There is also a predicted peak, A, of roughly half their intensities at about 740 nm, but this occurs where the experimental spectrum shows negligible absorption. Notwithstanding these discrepancies Spevacek and Spevackova stress the fact that the presence of two predicted lines in the visible (A and B) does not imply the presence of keto and enol forms. Although theory does not predict absorption at 16×10^{-3} cm^{-1} where the actual spectrum shows a maximum almost intense as that at 22×10^{-3} cm^{-1}, the authors assert that "the similarity between the experimental and calculated spectrum for the enol form shows that the structure of the molecule in cyclohexane is near to the structure of the thiol form (7)." Others might draw entirely opposite conclusions, and it cannot be said that this aspect of dithizone chemistry is settled. The fact that the spectrum of dithizone in chloroform remains substantially unchanged when the temperature is reduced from 20°C to −48°C does not necessarily point to the existence of a single species in solution, for it is equally consistent with transformations between different dissolved species of very similar spectra, which involve little or no change in entropy.[29]

For the practicing analyst these considerations are purely academic, for experience has shown that any rearrangements in solution, (e.g., when the thiol form is liberated in any organic solvent by acidifying a metal-dithizone complex or an aqueous solution of an alkali dithizonate) proceed at too high a rate to influence any analytical procedure.

C. The Solubility of Dithizone in Aqueous and Organic Solvents

Since dithizone has two potentially dissociable hydrogen atoms it is convenient to abbreviate its formula as H_2Dz. It is necessary to be watchful, however, for some authors use the abbreviation HDz and primary copper(II) dithizonate may appear as $Cu(HDz)_2$ or CuDz and secondary copper(II) dithizonate as CuDz or CuDz′.

Dithizone dissolves in concentrated mineral acids to give red-violet solutions (λ_{max} 520 nm in 60% sulfuric acid) containing its conjugate acid H_3Dz^+ (12). The spectrophotometric value $\{H^+\}\{H_2Dz\}/\{H_3Dz^+\} = 10^{4.55}$ reported by Akaiwa and Kawamoto[32] is in poor agreement with the value pK = −5.5 obtained by measuring the increased percentage of water-soluble H_3Dz^+ when dithizone is partitioned between CCl_4 and aqueous sulphuric acid of increasing concentration.[32]



Thione form

(3)

Thiol form

(6)

Conjugate acid

(12)

Yellow anion

(13)

If such concentrated solutions are left to stand (and more readily by heating a solution in glacial acetic acid) gradual oxidation takes place with the formation of a purple bicyclic compound 3-phenylazobenzo-1,3,4(4H)-thiadiazole.[33]

Although dithizone is practically insoluble in water below pH (solubility ∿5 × 10^{-5} g l^{-1}), it dissolves readily in alkalis to give the yellow anion (13) for which ε = 2200 m^2 mol^{-1} at λ_{max} 470 nm (cf. Figure 1). Such alkaline solutions are very prone to aerial oxidation.

Because of its low solubility in water it has proved difficult to obtain values for the acid dissociation constant of dithizone and it had to be derived from other measurements, e.g., from its partition coefficient (q.v.), or by extrapolation of spectrophotometric measurements in dioxan-water mixtures, or radiometrically.[3] The average for $K_r = \{H^+\}[HDz^-]/[H_2Dz] = 10.^{-4.47} \pm^{0.25}$

Although formally a diprotonic acid, dithizone does not readily dissociate its second proton below pH 14. Changes in absorption spectra (when the concentration of alkali was raised to 2.6 *M*) suggested to Spevacek and Spevackova the formation of the anion Dz^{2-} for which they calculated some spectra parameters; on the other hand Geiger and Sandell noted that similar changes in the 10 *M* KOH they used could have been caused by traces of silver.[34] The second proton is certainly labilized when the first has been replaced by a metal. Thus mercury(II) dithizonate, $Hg(HDz)_2$ dissolved in benzene is 99% N-deuterated to $Hg(DDz)_2$ simply by shaking with D_2O, and the proton can also be replaced by silver to give silver-mercury dithizonates.[3] *S*-Methyl dithizone, MeHDz (as 6), forms a series of metal salts such as CuCl(MeDz), PhHg(MeDz), and $Ni(MeDz)_2$, but the most convincing evidence is the behavior of the yellow complex of phenylmercury(II), which gives rise to a magenta colored anion:

$$\underset{\text{(yellow)}}{PhHg(HD_z)} \rightleftharpoons \underset{\text{(magenta)}}{PhHgDz^- + H^+}$$

In 52.8% (v/v) ethanol-water the value pK = 11.46 for this equilibrium was measured spectrophotometrically.[36]

Although sparingly soluble in water, dithizone is much more soluble in a variety of organic solvents and Table I summarizes (average) values for those that are most frequently used.

If dithizone is equilibrated with a mixture of an aqueous buffer and an immiscible organic solvent it will distribute itself according to the following relationship:[3]

$$D = \frac{\text{total concentration of dithizone in organic phase}}{\text{total concentration of dithizone in aqueous buffer}}$$

$$= [H_2Dz]_o/([H_2Dz] + [HDz^-])$$

$$= p_r/[1 + (K_r/[H^+])] \qquad (1)$$

where the partition coefficient $p_r = [H_2Dz]_o/[H_2Dz]$, the acid dissociation constant $K_r = [H^+]\,[HDz^-]/[H_2Dz]$, and the subscript o distinguishes a species in the organic phase. Since $K_r \sim 10^{-5}$, $K_r/[H^+] \gg 1$ above pH 7 and

$$\log D = \log p_r + pK_r - pH \qquad (2)$$

TABLE 1

Some Properties of Dithizone in Solution at 20 to 22°C

Solvent	Solubility (g l^{-1})	$pH_{1/2}$	Absorption spectra $\lambda_{max,1}$ nm	$\lambda_{max,2}$ nm	Peak ratio
Chloroform	17.6	10.62	605	440	2.59
			(4.14)	(1.59)	
o-Dichlorobenzene	1.7	9.37	622	452	1.90
			(3.48)	(1.83)	
Benzene	1.4	9.10	622	153	1.80
			(3.48)	(1.90)	
Toluene	1.0	8.97	622	450	
			(3.31)	(1.98)	1.68
Carbon tetrachloride	0.54	8.83	620	456	
			(3.46)	(2.03)	1.70.
Cyclohexane	0.014	7.42	623	452	
			(2.70)	(2.38)	1.13
Hexane	0.02	7.04	617	447	
			(2.76)	(2.541)	1.09

Note: The average values of solubility and $pH_{1/2}$ are taken from more extensive tabulations.[3] Molar absorption (extraction) coefficients given in parentheses are values of $10^{-3}\,\varepsilon\ m^2\ mol.^{-1}$

and when the reagent is 50% extracted such that $D = 1$ when $pH = pH;_{1/2}$

$$pH_{1/2} = \log p_r + pK_r \tag{3}$$

$$\log D = pH_{1/2} - pH = \Delta pH \tag{4}$$

Since the percentage extracted into the aqueous phase, $E = 100/(1 + D)$ function of pH, the plots of E vs. pH will take on a sigmoid form as shown in Figure 2 though they are represented explicitly by Equation 5.[3]

$$E = \frac{50(\coth 1.1513\,\Delta pH - 1 + 2p_r^{-1})}{(\coth 1.1513\,\Delta pH + p_r^{-1})} \tag{5}$$

The above expressions have used concentrations in place of activities, a simplification that appears to be adequate for all analytical work with dithizone: a more rigorous treatment is given elsewhere.[3,37] In the limit we can equate p_r with $S_{r,o}/S_r$, the ratio of the solubilities of the reagent in the organic and aqueous phase, and show that there exists a linear relationship between $pH_{1/2}$ and $\log S_{r,o}$ that takes the form[37]

$$pH_{1/2} = \log S_{r,o} + (pK_r - \log S_r). \tag{6}$$

Now the introduction of alkyl substitutes into the phenyl rings of dithizone decreases the solubility, S_r, in water and increases $S_{r,o}$ in the organic solvent (cf. Table 5 of Reference 3) and so enhances the values of $pH_{1/2}$. The (much less significant) increase in pK_r due to the introduction of an electron releasing group will act in the same way.[38]

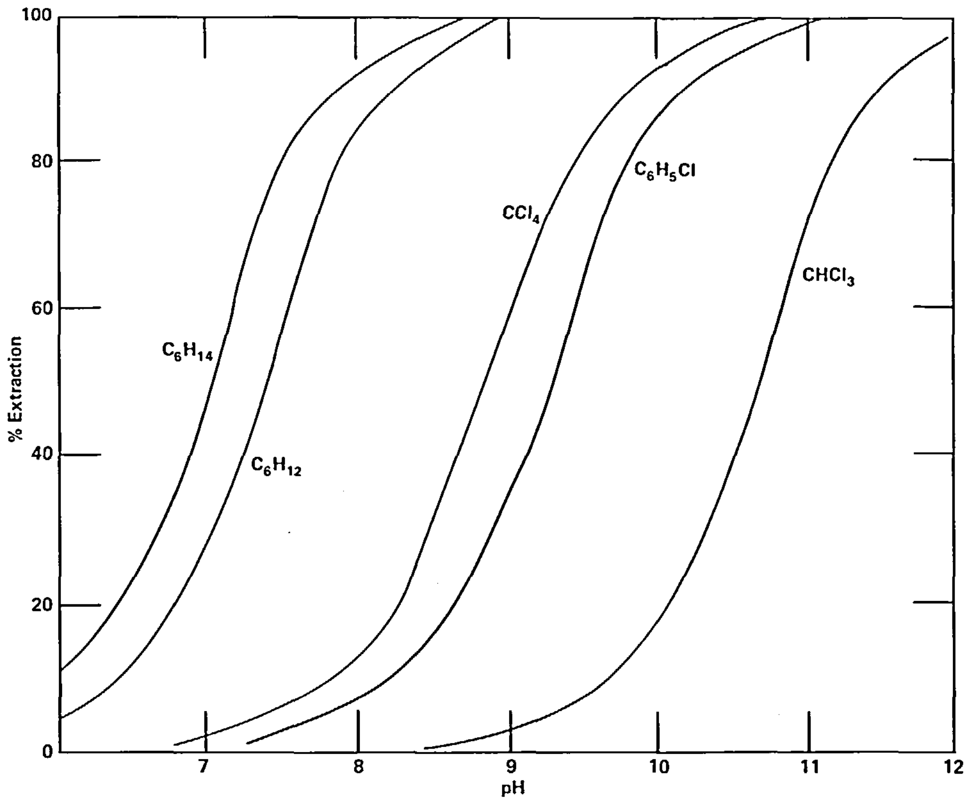
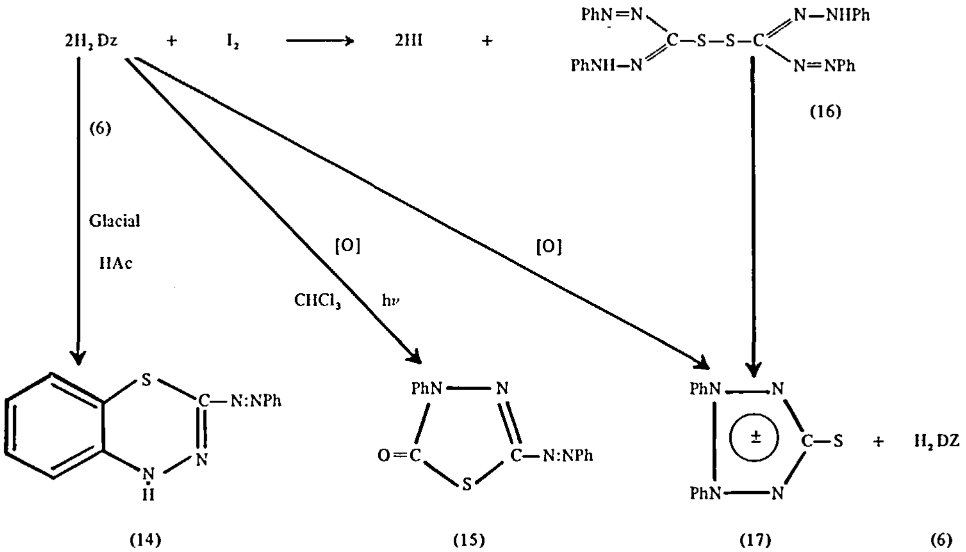


FIGURE 2. Sigmoid curves showing the effect of pH on the percentage of dithizone extracted from aqueous buffers into hexane, cyclohexane, carbon tetrachloride, chlorobenzene, and chloroform. Experimental points have been omitted in the interest of clarity.

It is not surprising then that the recently synthesized di-(*p*-butylphenyl)thiocarbazone with pK = 4.7 should have a value of $pH_{1/2}$ in chloroform about 15, and as high as 12.8 in hexane.[39] While this means that excess reagent cannot be stripped by alkali from a metal-dithizonate solution (q.v.) it also means that traces of metals can be stripped more efficiently from alkaline solutions.[39]

D. Deterioration of the Reagent and Its Solutions

When left to stand, more especially in sunlight or in warm surroundings, solutions of dithizone in organic solvents deteriorate more or less rapidly, the initial green-red color giving way to a pale brownish-yellow. This adverse feature becomes less disturbing and can be effectively eliminated by paying special attention to the purity of the solvents and the conditions of storage.[3,12] In bright sunlight chloroform photooxidizes to phosgene, which condenses with dissolved dithizone to give a yellow product (15) with maximum absorption at λ_{max} 375 nm (ε = 1930 m^2 mol^{-1}).[3,40] The most remarkable mode of decomposition is that produced by iodine and a whole range of other oxidizing agents.[40] In the presence of water, iodine brings about the expected oxidation of dithizone to the disulfide, bis-1,5-diphenylformazan-3-yl-disulfide (16), which, however. decomposes spontaneously by first order kinetics to give an equimolar mixture of dithizone and a mesoionic compound (17) previously prepared and commonly known under the name dehydrodithizone.



With the amount of oxidant shown above the visible effect is a rapid change in color from green to orange red, but since the rate of the disproportionate depends on the solvent (being fast in chloroform, but much slower in hexane) the reformation of (6) causes a more or less rapid return of the dithizone color. Clearly the composition of a decomposing solution will depend upon the solvent, the relative amounts of reactants, the time, and the presence or absence of sunlight.

As already stated the deterioration of stock solutions of dithizone can be retarded by using purified materials and avoiding direct sunlight and high ambient temperatures. Commercial samples of dithizone may well contain variable amounts of impurities, which include the "yellow oxidation product", itself a complex mixture. Many recipes have been published for preparing the pure material in solution or in solid form, but column or paper chromatography has the advantage of establishing the homogeneity of the separated purified reagent.[3,12,40,41]

III. METAL DITHIZONATES AND LIQUID-LIQUID EXTRACTION

A. Metal-Dithizone Complexes

The preparation of metal dithizonates in the solid state was first reported by E. Fischer and by Bamberger et al.,[25,26] but since then many other solid compounds have been described in individual research papers.[42] An even larger number have been identified only in dilute solution in liquid-liquid extraction procedures, although their compositions have been established by Job's method of continuous variations, by the method of slopes, by two-phase titrations, or by other methods (examples of which are fully described and illustrated in Reference 3).

Two classes of stoichiometric complexes can be distinguished: (a) those derived from the anion (13) and a cation M^{n+}, which have the formula $M(HDz)_n$, and *(b)* those richer in metal and derived from the dinegatively charged anion Dz^{2-} and the metal M^{n+} and having the formula $M_{2/n}Dz$. On the assumption that the former were derived by replacing an imino hydrogen of a thione form (3) by a metal (the sulfur surprisingly being assumed not to bond preferentially to heavy metals!) H. Fischer termed them keto-dithizonates and those of class (b) enol-dithizonates.[1] Nowadays the former are invariably termed primary dithizonates and the latter, secondary. With rare exceptions the secondary dithizonates play an insignificant role in analytical chemistry, and they will not be discussed further here despite the academic interest that attaches to their still uncertain structures.[3] Typical compounds of well-established composition are shown in Table 2.

All primary dithizonates are typical chelate compounds almost insoluble in water, reasonably soluble in chloroform, but much less so in CCl_4 and often poorly soluble in hexane. Though these properties favor liquid-liquid partition into an organic phase, the choice of solvents is limited by solubility factors — although this is less serious than might be thought at first sight, since the very high molar extinction coefficients (cf. Table 2) permit working with micro amounts under ordinary conditions. Other factors such as toxicity, cost, volatility, flammability, hazardism, rate of extraction, density relative to water, and ease of phase separation must enter into the final choice of solvent.[3,9] Chloroform is commonly used when extraction for removal is a primary aim, and carbon tetrachloride for ordinary purposes employing spectrophotometric finishes, while esters such as ethyl propionate and ketones such as acetone or hexone have advantages when isolating metal dithizonates for determination by atomic absorption spectroscopy.[43,44]

The structure of several metal dithizonates has been determined by X-ray crystallography.[3] Zinc and mercury(II) form tetrahedral, and copper(II), nickel, palladium(II), and platinum(II) give square-planar complexes. Those of silver, lead, and bismuth, etc. are still unknown, owing to the difficulty of obtaining suitable crystals.

B. Basic Principles of Dithizone Extractions

The various equilibria governing the extraction of primary dithizonates is shown diagramatically in Figure 3, which presents the simplified system in which no auxiliary complexing agents are present, and where no complexes between the cation M^{n+} and hydroxyl ions need be considered. K_r and p_r are the acid dissociation constant and partition coefficient of the reagent dithizone, while $\beta_n = [M(HDz)_n]/M^n] [HDz^-]^n$ is the overall stability constant of the metal dithizonate $M(HDz)_n$ and $p_c = [M(HDz)_n]_o/$ $[M(HDz)_n$ is its partition coefficient.

The fundamental equation for the extraction is

$$M^{n+} + nH_2Dz(org) \overset{K_{ex}}{\rightleftharpoons} M(HDz)_n(org) + nH^+ \qquad (7)$$

so that the important extraction constant $K_{ex} = [M(HDz)_n]_o[H^+]^n/[M^{n+}] [H_2Dz]_o^n$ Since we can assume that the term $[M(HDz)_n]$ is negligible the distribution ratio D will be given by

$$D = [M(HDz)_n]_o/[M^{n+}] = K_{ex}[H_2Dz]_o^n/[H^+]^n \qquad (8)$$

whence

$$\log D = \log K_{ex} + n(pH + \log [H_2Dz]_o) \qquad (9)$$

showing that the amount of complex extraction into the organic phase will increase with the pH and with the excess of reagent.

If the amount of excess reagent $[H_2Dz]_o$ is maintained constant extraction will reach 50% when $D = 1$ and $pH = pH_{1/2}$, the pH of half-extraction whence it follows that

$$\log K_{ex} + n(pH_{1/2} + \log [H_2Dz]_o) = \log 1 = 0 \qquad (10)$$

and

$$n\Delta pH = n(pH_{1/2} - pH) = -\log D = \log (100 - E)/E \qquad (11)$$

TABLE 2

Properties of Some Primary Dithizonates

Formula	Color of solid	Spectrum in solvent[a] λ/nm ($10^{-2} \times \varepsilon/\mathrm{m}^2\ \mathrm{mol}^{-1}$)					Color of dilute solution in CCl_4	Solubility[e] $10^2 \times S_{r,o}$/mol ℓ^{-1}	Extraction constant log K_{Ex}[f]
HDz	Black	300(9.2)	365(4.4)	450(20)	510(4.4)	620(33)	Emerald green	0.29, 7.93[b]	
		265(12)[b]	365(4.0)[b]	445(16)[b]	505(6.0)[b]	605(40)[b]	Blue green	0.5[b]	
Ag(HDz)	Orange red	273(17)	365(2.8)	462(30)			Golden yellow	0.4, 1.6[b]	6.5, 5.8[b]
Tl(HDz)	Dark red			515,615sh			Raspberry red		−3.7
		225(21)[b]	400(2.8)[b]	505(33)[b]					
$Co(HDz)_2$[c]	Black	272(36)	370(11)	542(59)			Violet-red	0.02, 0.2[b]	1.5
$Ni(HDz)_2$	Dark purple	282(35)	385(14)	480(30)	630(16)	665(19)	Violet brown	0.1, 0.2[b]	−0.9
$Cu(HDz)_2$[d]	Black	280(25)	350(15)	550(45)			Red-violet	0.055	~10
				545[b]				0.2[b]	8.5[b]
$Zn(HDz)_2$	Green	280(31)	420(5.6)	536(92)			Purplish red	0.125	1.7
		280(34)[b]	420(5.2)[b]	532(88)[b]			Purplish red[b]	3.65[b]	−1.5[b]
$Cd(HDz)_2$	Orange-brown	280(34)	410(4.8)	520(88)			Pink	0.001	~1.8
		280(35)[b]	405(4.8)[b]	520(86)[b]			Pink[b]	0.01[b]	0.5[b]
$Hg(HDz)_2$	Dark red	265(38)	375(5.2)	485(72)			Orange	6.007, 0.03[b]	26.9
$Sn(HDz)_2$	Red	265(38)	395(8)	520(54)			Red		−2
$Pb(HDz)_2$	Red	270(35)	405(8)	520(69)			Carmine red	0.002	0.4
		275(37)[b]	405(8)[b]	518(64)[b]			Carmine red[b]	0.04[b]	−0.9[b]
$Pd(HDz)_2$[d]	Purple	280(38)	370(8.0)	450(34)	500(19)	640(29)	Green	0.05	42.5
$Pt(HDz)_2$	Black	260(30)	370(7.6)	490(32)	570(5.6)	710(3)	Brownish yellow		
$Bi(HDz)_3$	Green	275(60)	380(14)	490(80)			Red-orange	0.087, 0.01[b]	10.0,8.7[b]
$In(HDz)_3$	Brown	275(36)	385(12)	510(87)			Raspberry red	0.08, 0.1[b]	4.8, 0.6[b]

[a] Data mainly from References 3 and 12 given in order λ_{max}, λ_{min}, λ_{max}, etc. Literature values of λ and more especially of ε are often very inconsistent; see text.

[b] Data for CCl_4.

[c] The formula has been disputed; see text.

[d] Differently colored products have been reported,[42] but the behaviors in ordinary procedures are quoted here.

[e] Many of these are clearly rough estimates,[12] but others have been carefully determined; see Table 13 of Reference 3.

[f] See Table 11, Reference 3. Starý and Freiser's compilation should be consulted.[38]

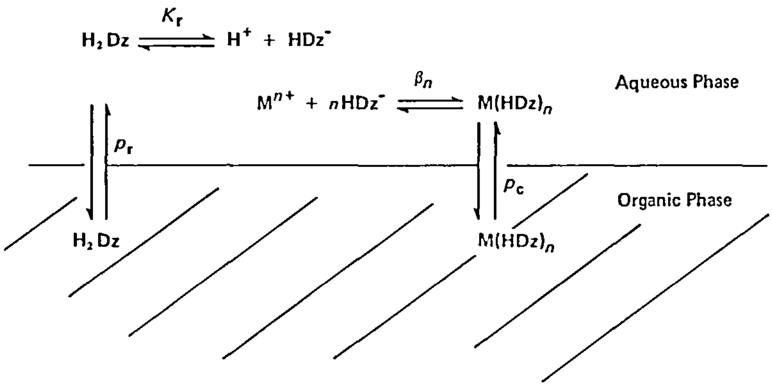


FIGURE 3. Equilibria in a two-phase system involving cations, M^{n+}, dithizone, H_2Dz, and a primary metal dithizonate, $M(HDz)_n$, in the absence of auxiliary complexing agents.

where E is the percentage of metal extracted into the organic phase. It follows that

$$E = 50(1 - \tanh 1.1513 n \Delta pH) \qquad (12)$$

so that plots of E against pH will be sigmoid and centrosymmetric about the midpoint ($E = 50\%$, $pH = pH_{1/2}$) as shown in Figure 4, which is drawn for the point of illustration only.

Suppose we are dealing with the extraction of a particular metal dithizonate, $M(HDz)_2$, for which $K_{ex} = 2.0$ and $n = 2$. Then curves ABC, DEF, GHI, and JKL for which $pH_{1/2} = 2,4,6$, and 7 would describe extraction when $[HDz]_o = 10^{-3}$, 10^{-5}, 10^{-7}, and 10^{-8}, respectively. As the concentration of excess dithizone decreases, the pH has to be increased in accordance with Equation 9: a decrease of one unit of pH requires a tenfold increase in the concentration of ligand in excess. Solubility considerations give an upper limit to the concentration of dithizone, but the value of pH is easily adjusted over a range of at least 14 units.

The slope of the sigmoid curve is given by $dE/dpH = 57.57\, n\,(1 - \tanh^2 n\, \Delta pH)$ and the slope at the midpoint will be $57.57\, n\%$ per pH unit. This means that the higher the valency of the metal, the steeper the slope. This is illustrated in Figure 4 by the curves MEN, DEF, and OEP drawn for $pH_{1/2} = 4$ and $[H_2Dz] = 10^{-6}$ in each case and the dithizonates with $n = 1$ ($K_{ex} = 10^2$), $n = 2$ ($K_{ex} = 10^4$) and $n = 3$ ($K_{ex} = 10^6$), respectively. There is an effect of practical consequence, for as n increases the adjustment of the pH for a given amount of extraction becomes more critical. Explicitly the pH range for 1.0 to 99.0% extraction would be 4 units ($pH_{1/2} \pm 2$) when $n = 1$, 2 units ($pH_{1/2} \pm 1$) when $n = 2$, and only 1.34 units ($pH \pm 0.67$) when $n = 3$.

Finally consider the simultaneous extraction of four different divalent metals W($K_{ex} = 10^4$), X($K_{ex} = 10^2$), Y($K_{ex} = 10^{-2}$) and Z($K_{ex} = 10^{-4}$) with sufficient dithizone to give an excess $[HDz]_o = 10^{-5}$ *M*. The theoretical extraction curves will be represented by ABC, DEF, GHI, and JKL, respectively. If all the metals were present in equivalent amounts we would predict at pH 6 the complete extraction of W and X, 50% extraction of Y, and negligible extraction of Z. Above this pH the extract containing A and B would be increasingly contaminated by Y and Z; below this pH the extraction of X would become increasingly incomplete. It must be emphasized that these theoretical

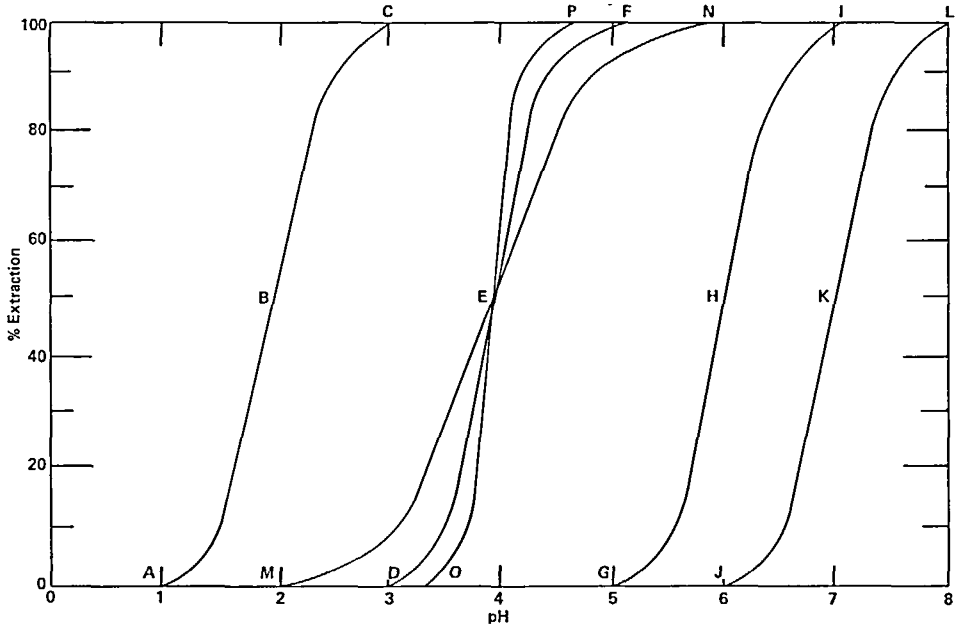


FIGURE 4. Sigmoid curves showing how increase of pH increases the percentage extraction for primary dithizonates of different composition (curves MON, DEF, and OEP) or different values of K_{ex}, or with different amounts of excess dithizone, $[H_2Dz]_o$. For details see text.

curves refer only to *percentage* extractions. If a mixture of 2 μg of X and 1000 μg of Y were to be extracted at pH 3.5, the organic extract would contain 99.9% of X (1.998 μg) and 9.1% of Y (91 μg). The degree of contamination has certainly been reduced from Y/X = 500/1 to 45/1, but it is still considerable. By extracting at pH 3 the relative amounts of Y and X would be 10 μg and 1.98 μg, so that less contamination by Y must involve a lower recovery of X.

There is a limit to which any separation can be improved by adjusting the pH, for it must not be forgotten that in addition to reducing $[H^+]$ and so favoring the right hand side of Equation 7, raising the pH also implies adding hydroxyl ions which can compete with dithizonate ions as auxiliary complexing agents. Thus the percentage extraction of amphoteric metals such as zinc, lead, and tin(II) rises to a maximum and then falls off as the pH increases. Another effect is the undesirable formation of extractable secondary complexes such as CuDz or Ag_2Dz or PdDz or hydroxy complexes such as HO·Hg(HDz).[3]

Clearly the most effective separations will be those where the magnitudes of K_{ex} are most widely different and optimum conditions are well discussed elsewhere.[22] It was realized empirically by Fischer that separations could be made more efficient by the use of auxiliary complexing agents — masking agents — for by reducing the concentration of free metal ions, $[M^{n+}]$, they effectively increase K_{ex} — and do so selectively. Table 3 shows some typical observations and the range and variety of separations could be extended and diversified by consulting a table of metal-ligand stability constants.[3]

The above considerations apply equally to the extraction and separation of primary dithizonates derived from organometallic cations such as $ArHg^+$, $(CH_3)_2Tl^+$, $(C_6H_5)_3Pb^+$, R_2Sn^{2+}.[3] For such systems there have been relatively few measurements of the extraction constants K_{ex} although the pH range for optimum extraction is usually reported (cf. References 3 and 12 and details therein).

TABLE 3

The Application of Auxiliary Complexing (Masking) Agents in Improving the Separation of Metal Dithizonates in Liquid-Liquid Extractions

Conditions	Metals that still react with dithizone
Slightly acidic solutions	
Containing cyanide	Pd(II), Ag, Hg(II), Cu(II)
Containing bromide or iodide	Au, Pd(II), Cu(II),
Containing thiocyanate	Au, Hg(II), Cu(II)
Containing cyanide and thiocyanate	Hg(II), Cu(II)
Containing thiosulfate at pH ~5	Pd(II), Zn, Sn(II), Cd
Containing thiosulfate and cyanide at pH 4—5	Zn, Sn(II)
Containing EDTA	Ag, Hg(II)
Basic solutions	
Basic solutions containing cyanide	Tl(I), Sn(II), Pb, Bi
Slightly alkaline solutions containing bis-(2-hydroxylethyl)-dithiocarbamate	Zn
Strongly alkaline solutions containing citrate or tartrate	Ag, Tl(I), Co, Ni, Cu(II), Cd

C. Spectrophotometric Finishes

When a metal has been extracted according to the above principles, the organic phase will contain its primary metal dithizonate together with more or less excess reagent and its spectrum will be a superimposition of the two. (We shall not consider here the behaviors of secondary dithizonates formed when the metal is in excess and the solution is more alkaline.) Fortunately the spectrum of most metal dithizonates is maximal where that of the reagent is small — but not usually negligible (cf. Figure 1). At the long wavelength maximum for dithizone the absorbance of most metal dithizonates is very small (cf. Figure 1). If a spectrophotometric finish is desired, several alternates present themselves.

1. Monocolor Method

In the *Monocolor method,* excess reagent is stripped from the organic extract by shaking with dilute ammonia, a procedure permissible because of the high stability of most metal dithizonates to moderately high pH and to favorable kinetic factors in others. The absorbance of the residual metal dithizonate is then measured as its λ_{max}.[3,12]

2. Mixed Color Method

In the *mixed color method* the contribution to the absorbance at λ_{max} (metal complex) from excess dithizone can be allowed for by measuring its absorbance at λ_{max} (reagent) where ε (reagent) $\gg$ ε (complex) and computing what it would be at λ_{max} (complex) from a knowledge of the relevant extinction coefficients.[3] Alternatively the amount of desired metal dithizonate can be derived from a series of calibration curves made for mixtures of metal and reagent covering a sufficiently wide range of compositions, or by solving the two linear equations relating the two absorbancies measured, respectively, at λ_{max} (complex) and λ_{max} (reagent) and the four relevant molecular extinction coefficients.[3]

The principal can obviously be extended to ternary or higher systems. For example, a rapid spectrophotometric determination of mixtures of di- and tri-alkyl-lead(IV) salts and inorganic lead(II) can be carried out by extracting them together as a mixture of dithizonates, $Et_3Pb(HDz)$ (canary-yellow, λ_{max} 435), $Et_2Pb(HDz)_2$ (orange, λ_{max} 487), and $Pb(HDz)_2$ (red, λ_{max} 520) into chloroform, measuring the absorbancies at 424, 500, and 540 nm, and solving the three simultaneous equations by using predetermined values of all the necessary (six) molecular extinction coefficients.[46] If the sample contains Et_4Pb as well, treatment with iodine in an ammonia buffer produces an equivalent amount of Et_3PbI and a redetermination of the mixed alkyls as above gives the concentration of tetraethyllead by difference.

3. Reversion Method

A possible drawback to these procedures is the presence in solution of adventitious amounts of absorbing material, e.g., from an impure or deteriorating sample of dithizone. In the *reversion method* [3], we first measure the absorbance of the organic phase, which may contain colored impurities (concentration c_i, extinction coefficient ε_i), excess dithizone (concentration c_r, extinction coefficient ε_r), and various metal dithizonates (c_d, ε_d) in addition to that of the metal being determined ($[M(HDz)_2] = c_M$, extinction coefficient ε_M). We have

$$A = 1(c_M\epsilon_M + c_r\epsilon_r + \Sigma c_d\epsilon_d + \Sigma c_I\epsilon_I) \qquad (13)$$

The extract is then treated with a "reversion reagent" chosen because it reacts selectively and quantitatively with the desired metal dithizonate only, liberating metal ions that pass into the aqueous phase and an equivalent amount of dithizone that passes into the organic phase. Thus

$$\text{reversion agent} + \underset{c_M}{M(HDz)_n} \rightarrow M^{n+} + \underset{n\,c_M}{n(H_2Dz)} + \ldots\ldots \qquad (14)$$

The new absorbance will be

$$A_r = 1(nc_M\epsilon_r + c_r\epsilon_r + \Sigma c_d\epsilon_d + \Sigma c_I\epsilon_I) \qquad (15)$$

and the "reversion value"

$$R = A_r - A = 1c_M(n\epsilon_r - \epsilon_M) \qquad (16)$$

is linearly proportioned to the concentration of the metal dithizonate and thus to that of the metal being determined. If measurements are made at λ_{max} for dithizone (where $\varepsilon_r \gg \varepsilon_M$) the calibration curve will be linear and pass through the origin. It is convenient to measure A_r against A with the unreverted solution in the reference cell; this gives R directly.[3] The method has recently been applied to the determination of lead and bismuth in high-purity tellurium.[47]

Ashizawa et al. have recently reexamined the monocolor procedures for lead, zinc, and cadmium in considerable detail.[48] Other spectrophotometric finishes are still very commonly applied, as will be seen in the procedures discussed element-by-element later in Section IV.

The systematic application of dithizone to the determination of several trace metals in the same sample is well illustrated by the analysis of rhenium for bismuth, cadmium, copper, lead, thallium, and zinc,[49] and even better by the determination, all by spectrophotometric procedures, of cadmium, cobalt, copper, lead, nickel, and zinc in silver halides.[50]

D. Other Separation Processes

1. Thin Layer Chromatography (TLC)

A great deal of work on paper and column chromatography up to 1970 is reported in some detail in Iwantschaff's book.[12] Work in the last decade has emphasized the current trends towards the separation and identification of even smaller quantities and the manipulation of the complex mixtures obtained in environmental studies.

Muchova and Jokl separate about 17 common cations by TLC after complexing with oxine, diethyldithiocarbamate, or dithizone,[51] and report the R_f values.[52] Massa separated cadmium from zinc in pharmaceutical preparations by chromatographing the extracted dithizonates and determining the concentration of $Cd(HDz_3)_2$ directly on the chromatogram by reflectance photodensitometry.[53] The same technique was employed by Takitani et al. who first extracted Cu(II), Hg(II), and Pd at pH 0 to 1 and Bi, Co, Ni, Pb, and Zn at pH 7 to 8 before TLC and densitometry; relative standard deviations ranged from 0.9 to 9.8%.[54] In examining total metals in water by this technique, using dithizone in combination with other reagents, Ce, Cu, Fe, and Hg were identified down to 0.1 ppm, Bi, Co, Mn, Ni, Pb, Sn, and Zn, down to 0.5 ppm, Al and Be down to 1 ppm and Cr to 8 ppm.[55]

Sebesta used the technique to separate a number of radioactive isotopes,[56] and Gregorowitz et al. detected 0.03 to 0.3 μg of Bi, Cd, Co, Cu, Pb, and Zn.[57] By using a layer of Al_2O_3 only 1 to 6 μm thick, produced by anodic oxidation of aluminum film or wire, less than 1 ng of metal dithizonates can be separated.[58] A most detailed study of the effect of different eluents on the separation of mixtures of metal dithizonates by TLC suggests that the best procedure is to allow that solvent front to reach a predetermined spot, remove the chromatogram, dry and rerun, optimally for about four times.[59] Quantitative determinations can then be made by treating the 5 *M* HCl and determining the liberated dithizone spectrophotometrically. Overall losses were carefully examined.[60]

Organomercurials, RHg^+ (R = Me, Et, $MeO \cdot C_2H_4$, $EtO \cdot C_2H_4$, C_6H_5, $(Ch_3 \cdot C_6H_4)$ in fungicides can be separated as dithizonates on a variety of substrates,[61] and dithizone is an excellent spray reagent for developing colors, (e.g., R_4Sn, blue; R_3Sn^+, ochre yellow; R_2Sn^{2+}, RSn^{3+}, and Sn^{4+}, carmine orange-red) after TLC of organotin compounds.[62] Hg^{2+} and RHg^+ (R = 1 to 18 carbon atoms) can be separated as their dithizonates by reversed phase TLC with amounts in the range 0.07 to 0.1 μg visually detectable.[63]

2. Column Chromatography

Busev et al. have examined the potentialities of solid absorbents, (e.g., $CaCO_3$, Na_2HPO_4, Na_3MoO_4, $Na(K)HCO_3$, Na(K) citrate, etc.) for the separation of metal dithizonates and reported orders of elution and the effect of particle size. Separation of mixtures such as Cd-Zn, Cd-Pb, Cd-Bi, Zn-Bi, and Pb-Bi are described.[64,65]

Reversed phase chromatography with silicone treated chromosorb W-HP columns coated with dithizone dissolved in *o*-dichlorobenzene have been used for concentrating trace metals and for the separation of zinc (100 μg) from a 10^5-fold excess of cadmium.[66] Spěváčková and Křivánek used the same principle for the separation of Bi, Cu, Hg, In, Mn, Ni, Pb, and Zn, for the separation of iron-59 from cobalt-60 and the determination of Cu, Fe, and Zn by activation analysis.[67]

Correlations between K_{ex} and mobility and between cation electro-negativity and R_m values have been examined in theoretical studies by Gallik,[68] and by Bauman and Richards who concluded that the metal dithizonates are probably a heterogeneous group of compounds that differ in coordination configuration and geometry.[69]

IV. A SURVEY OF RECENT LITERATURE

In this chapter we shall summarize information published mainly in the last 10 years, which deals with primary metal dithizonates and their applications. Particular applications, e.g., in atomic absorption spectroscopy, in neutron activation analysis, for ion-selective electrodes, and for substoichiometry will be considered again later on, together with a number of other general topics.

The elements are dealt with in alphabetical order. So far as well-established procedures are concerned, nothing can replace the detailed accounts given in Iwantscheff's book,[12] and the following comments do not attempt to do more than indicate the scope of later work.

A. Antimony

The extraction of antimony(III) by H_2Dz/CCl_4 in the form of $Sb(HDz)_3$ has been confirmed by Shoji et al.[70] By using antimony-124m, Kamada and Yamamoto found that antimony(V) is not extracted by dithizone (0.03%, w/v) at pH 4, but with antimony(III), 57, 38, and 8% were extracted by hexone, nitrobenzene, and carbon tetrachloride, respectively. With 5 *N* acid the values for hexone were 52% (HCl) and 2% (H_2SO_4) for antimony(III) and 42% (HCl) and 0% (H_2SO_4) for antimony(V); less was extracted by nitrobenzene and nothing by CCl_4.[71] The nature of the extracted species was not studied.

B. Arsenic

The extraction of arsenic(III) from 3 to 7 *M* HCl, probably in the form $Cl_2As(HDz)$ or $ClAs(HDz)_2$ was reported a long time ago.[12] A mixed dithizonate, AsDz(DDC), obtained as follows

$$\mathrm{As(DDC)_3 + 2Ag(HDz) \rightarrow AsDz(DDC) + 2AgDDC + H_2Dz} \qquad (17)$$

forms the basis of a new spectrophotometric procedure. The arsenic is first extracted at pH <5.5 with sodium diethyldithiocarbamate (NaDDC) and treated with a tenfold excess of silver dithizonate and the amount of dithizone liberated (λ_{max} 600 to 620 nm) is proportional to the amount of arsenic.[72]

C. Bismuth

After a preliminary extraction of bismuth and lead from high-purity tellurium by H_2Dz/CCl_4 the lead dithizonate is reverted by NH_4Cl at pH 3.5 and lead and bismuth determined spectrophotometrically.[47] Levitman et al. compared the accuracy and precision for the determination of bismuth by eight reagents and found dithizone to be the most sensitive with a relative error of 0.25% for the determination of 0.0753 mg.[73] Chromatographic separations have frequently been reported.[54-57,60,64-67]

D. Cadmium

Well-established methods[12] are used as a basis for determining small amounts of cadmium in organic matter,[74] or in waste waters containing large amounts of zinc and manganese after a preliminary extraction of iodides into isobutylmethylketone (hexone),[75] or after concentration as $Cd(CN)_2^{2-}$ on an anion-exchange resin,[76] or after separation as cadmium metal by sublimation from impure cadmium sulfide at 520°C.[77]

Both cadmium and zinc can be leached from soils by 0.1 *M* $CaCl_2$ containing 0.5 *M* sodium acetate and 10% hydroxylamine hydrochloride at pH 4.5, and determined after extraction with H_2Dz/CCl_4 followed by AAS.[78] Substoichiometric determinations have also been used for cadmium,[79] and nanogram amounts in high purity MoO_3 and WO_3 can be concentrated on a column of siliconized Chromosorb® W-HP loaded with dithizone dissolved in *o*-dichlorobenzene, separated by reversed-phase chromatography and determined with high precision by AAS or flameless AAS.[66,80] Many separations involving TLC have been reported.[51,53,55-57,60,64-67]

E. Cobalt

The very slow rate of extraction of cobalt dithizone has been an inconvenient feature that can be overcome by the addition of pyridine, although the reasons for this are not established.[81] Certainly the spectrum of the dithizone extract is different in the presence of this ligand.

The age old controversy as to whether the species extracted is $Co(HDe)_2$ or $Co(HDz)_3$, containing cobalt in oxidation state 2 or 3,[3,12] would seem to be resolved by Kemula et al. who determined the metal content electrolytically.[82] Treatment with Ag^+ gave two equivalents of Ag(HDz), but the third organic residue was oxidized, pointing to a complex of cobalt(III) in agreement with the observed absence of paramagnetism.[3,29] Chromatographic separations, especially by TLC are well documented.[51,54,55,57,60,65,67]

F. Copper

Only small improvements on well-established procedures[12] appear in a recent spectrophotometric determination of small amounts of copper in tin oxide,[83] or in biological materials,[84] where the authors use benzene and heptane as solvents for the extractant.

The difference in the amount of copper found in seawater by dithizone extraction before and after oxidation with perchloric acid is attributed to organically bound copper.[85] Dithizone extraction has been used to remove metals from rocks and sediments after digestion with HF, H_2SO_4, and $HClO_4$. Copper and zinc can then be stripped (back-extracted into an aqueous phase) with dilute HCl and determined by AAS.[86] In another procedure copper (0.14 to 4.2%) and bismuth (0.066 to 0.66%) can be extracted selectively in the presence of citrate or cyanide, respectively. In this case the metal is recovered by oxidizing the organic extract with a solution of CrO_3 in acetic acid and determined by biamperometric titration with dilute EDTA.[87]

An unusual use of dithizone is made in determination of silver or copper (0 to 0.1 ppm) in high-purity lead or zinc. The addition of 0.4% H_2Dz in ethyleneglycol monomethyl ether to a solution containing the trace elements in 0.1 M HNO_3 in a flotation cell gives solids that can be floated off in nitrogen — and after being collected and washed, dissolved in acetone and determined in some suitable manner.[88] A preliminary dithizone extraction is used to remove copper from nickel and cobalt salts,[89] food and commodities,[90] rocks and sediments,[86] and high-purity oxides of Mo and W,[80] prior to determination by AAS. The ubiquitous occurrence of copper has led to many studies of its chromatography in the form of its primary dithizonate.[51,54,55,57,58,60,65,67]

G. Gallium

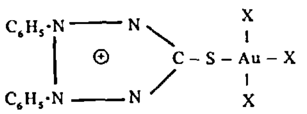
Iwantscheff and Jörrens observed that although gallium(III) does not readily form a stable dithizonate, the complexes $R_2Ga(HDz)_2$ (where R = Et, Pr, Bu, and iso-Bu) are extractable into CCl_4 or $CHCl_3$ over a wide pH range and indeed withstand shaking with 2 N ammonium hydroxide or 2 N hydrochloric acid. $GaCl(HDz)_2$ and *n*-$BuGa(HDz)_2$ are among complexes (λ_{max} 530 to 550, ε_{max} 4000 to 5100 $m^2\ mol^{-1}$) that may assume some analytical importance.[91]

H. Gold

Up to 1968 at least a score of papers had been published dealing with the determination of gold with dithizone,[12] for there is no doubt that when a solution of this reagent in an organic solvent is shaken with gold(III) salts a color develops which, under different authors' conditions, has been variously described as lemon-yellow, yellow, golden-brown, red, red-brown, and even violet, and with absorption maxima reported as 450, 460, and 605, 540 and 570, ~400 (sh.520), 450, 460, 550, and 570, 438 and 570 nm.[92] The molar ratio of gold to dithizone has been variously reported as 1:1, 1:3, 2:1, and 2:3 and some authors give the formula of the extractable species as $Au(HDz)(OH)_2$ and $Au(HDz)Cl_2$ on the basis of the analysis of solid samples.[42]

Beardsley et al. surveyed the situation in 1966 and concluded that gold reacted with dithizone to give a red-brown (1:1) complex and a yellow (2:1) complex, both extractable into chloroform. However, the proportions depended critically on a number of factors and they recommended that dithizone should not be used for the determination of gold — either by spectrophotometry or by extractive titration.[93] Russian workers in this field noted that the extraction of gold(III) was more complete if certain anions were present and postulated the extraction of ion-association complexes of the type $Au(HDz)_2^+X^-$ ($X = Cl, ClO_4, CCl_3{\cdot}COO$) or $Au(HDz)X_2$; with substoichiometric amounts, gold might be present as Au(I) (HDz) or $Au(HDz)Cl_2$.[216]

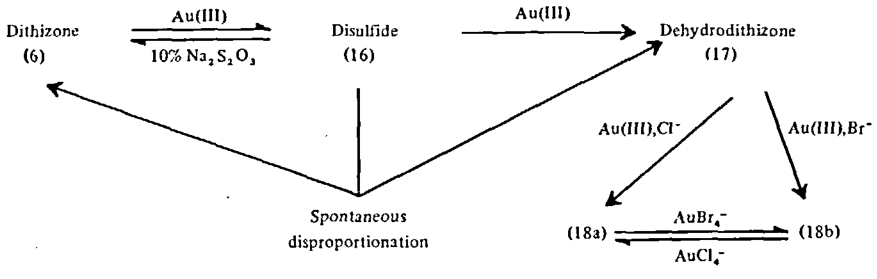
It remained for Cox and Servant to make a most thorough study of the system gold-dithizone that had led to so many discrepant observations.[96] They first showed that the reaction was essentially oxidative in character, the mixture of products depending upon the concentration in the aqueous phase of gold(III), of halide ion, of hydrogen ion, and on the duration and vigor of extraction.[92] Precisely the same factors had been found operative in the reaction between thallium(III) and dithizone.[29] All the observations of previous workers could be reproduced by appropriate alterations of conditions. The product absorbing at about 420 nm generated from aqueous gold(III) (6×10^{-3} *M*), chloride (0.775 *M*) and dithizone 8.4×10^{-5} *M* in chloroform was shown to be the gold-free bis-(1,5-diphenylformazan)-3-yl-disulfide (16), which is characterized by its ability to undergo disproportionation spontaneously into dithizone (6) and the mesoionic compound "dehydrodithizone" (17). It is clear that the yellow product λ_{max} ~420 attributed by earlier workers to "gold dithizonate" must have been this gold-free compound. If the disulfide is produced in the presence of excess gold(III) the absorbance at 420 nm decreases, while that at 240 and 320 nm increases (or at 260 and 390 if bromide replaces chloride). The actual extraction of gold arises because of this secondary reaction and by using gold-198 and chlorine-36 the extract was shown to be a complex of dehydrodithizone, gold, and halide ion in the molar proportions 1:1:3 with the probable formula



(18a; X = Cl

18b; X = Br)

The interaction of gold(III) with dithizone under weakly acid conditions can be summarized thus:



It appears probable that the complex situation arising in the extraction of other powerfully oxidizing cations (Se(IV), Te(IV), Tl(III), q.v.) may follow similar paths.

I. Indium

In addition to the well-studied $In(HDz)_3$,[12] $Et_2In(HDz)$ is said to form a red-violet complex (ε_{max} 4500 m^2 mol^{-1} at 520 nm in benzene), but no recent work has been reported on this element apart from its separation by reversed phase chromatography.[67]

J. Iron

Early work on the reactions of iron(II) and iron(III) with dithizone suggested that the former gave an unstable complex, while the latter caused oxidation only. It now appears that with iron(II) the species $Fe(HDz)_2$ can be extracted at pH 7.1 to 9.2 (CCl_4) or 7.8 to 9.5 ($CHCl_3$) to give a species with λ_{max} 580 nm and ε_{max} 5000 m^2 mol^{-1}, but since it is "unstable with time" it seems unlikely to find much application in quantitative determinations.[97] On the other hand Co^{2+} forms a stable complex over the range pH 4 to 13, whereas Fe^{3+} does not, so that a good separation of iron-59 from cobalt-60 is easily achieved.[67]

In the case of ion(III) extraction can be effected by dithizone in the presence of certain large anions and the ion-pair $Fe(HDz)_2^+X^-$ (where X = tetraphenylborate, caproate, perrhenate, etc.) can be extracted into chloroform or isoamyl alcohol prior to the determination of iron by AAS.[98] References to chromatography are naturally few in number.[51,55,57]

K. Lead

Despite the extensive literature on the determination of lead using dithizone (which had accumulated up to 1969)[12] many papers continue to be published reflecting both the continued importance of this element in health and environmental studies, and the change from a photometric finish to other procedures.

Airborne lead ($\leq$0.8 mg m^{-3}) collected on a filter paper can be taken up in HNO_3-H_2O_2 and $Pb(HDz)_2$ extracted with H_2Dz/toluene. Visual matching against standards provides a quick (15 min) field method.[99] In similar studies in German cities, Heller and Kettner noted that reagent blanks were due mainly to the release of lead from the glassware.[100] The reversion technique was used in the determination of lead and bismuth in high-purity tellurium,[47] and Oelschlager and Schwarz recognized that bismuth was the most serious source of interference when determining lead in biological substances.[101] Significant errors in direct AAS were overcome by a preliminary dithizone extraction and led to values comparable with the dithizone method.[102] Pierce and Meyer independently reported that the relative accuracy of AAS was higher as compared with the wet chemistry (dithizone) procedure, but the advantage was not statistically significant at the 0.05 level.[103]

AAS has been the preferred finish for the determination of lead in cast iron and steels,[43] in blood,[104] in lipsticks,[105] and in petroleum products.[106] On the other hand, a polarographic finish is used in studies by Karbainov and Stromberg,[107] while stripping voltammetry has also been employed.[108,109]

Florence and Batley used the dithizone method in deducing the chemical forms of lead and other heavy metals in seawater,[77] whereas Shendrikar and West employed it in conjunction with the ring-oven technique for determining lead in the range 0.05 to 1.0 μg.[110]

Postlethwaite et al. determined both lead (0.0005 to 0.05%) and bismuth in steel by a spectrophotometric dithizone procedure,[111] and Benini and Covella used $Pb(HDz)_2$ also for a spectrophotometric finish after a preliminary extraction of lead from urine using iodine/methylisopropyl ketone.[112]

The partition of $R_2Pb(HDz)_2$ between toluene and water at various pH values and other properties of the systems have been investigated for $R = C_nH_{2n+1}$, $n = 1$ to 6; in each case λ_{max} ~485 and values of ε_{max} increased with n.[113]

Hancock and Slater have devised a specific method for traces of $PbMe_4$ and $PbEt_4$ in the air. Treatment with iodine chloride in HCl transforms the tetraalkyls into the corresponding dialkyl salts, which are extracted with dithizone and determined by AAS (carbon rod furnace): determinations ranged from 0.2 down to 0.04 $\mu g\ m^{-3}$.[114]

Many chromatographic separations and determinations have been described.[51,54-58,60,64-66]

L. Manganese

It has long been known that manganese can be extracted by dithizone over the optimal ranges pH 9.5 to 11.0 ($CHCl_3$) or 9.0 to 10.3 (CCl_4) to give a violet complex, $Mn(HDz)_2$, λ_{max} 515 nm in $CHCl_3$, but even when the reagent is in large excess no more than 50 to 60% is extracted.[12,115] Akaiwa showed that the addition of pyridine had a marked synergistic effect,[115] and Marczenko and Mojski exploited this and found that in the presence of 0.6 *M* pyridine and a tenfold excess of dithizone the species $Mn(HDz)_2py_2$ (λ_{max} = 510 nm) was extracted over the range pH 8.5 to 10.2 The procedure was tested on the determination of manganese in sodium chloride and in high-purity tin; only thallium(I) interferes.[116] A few chromatographic separations have been reported.[51,55,67]

M. Mercury

In view of the increased public sensitivity to the toxiological hazards of mercury and especially organomercuricals, it is scarcely surprising that publications dealing with many analytical aspects have become available in great numbers. Some exploit new aspects of the use of dithizone, but many represent applications or minor modifications of well-tested procedures.[174] For example spectrophotometric determination of extracted mercury dithizonate is used in a classical procedure for the analysis of human organs,[117] and Naito et al. describe how the dithizone extract is freed from Ag, Cu, Bi, or Sn before photometry.[118] Papalou determined mercury compounds in waste waters after stripping excess dithizone with NaOH.[119] Pakter concentrates mercury in the air on activated MnO_2, displaces this by heating at 900°C and collecting in acidified permanganate prior to spectrophotometric determination as $Hg(HDz)_2$.[120] Ohta and Terai collect mercury in acidic hot springs by coprecipitating on cadmium sulfide. After taking up in nitric acid and adjusting to pH 4.5 copper is extracted with TTA prior to the spectrophotometric determination of $Hg(HDz)_2$.[121] In a departure from normal practice, Macovschi and Nitu use acetone as a solvent for dithizone and determine mercury ($\leqslant 50\ \mu g$) in the monophase from the absorbance of uncomplexed dithizone at 605 nm. The sensitivity is said to be $\sim 5 \times 10^{-4}\ g\ \ell^{-1}$.[122]

A recent paper asserts that the extraction of mercury at trace concentrations is incomplete and hindered by certain anions, that the complex is unstable within the period of measurement, and that the absorption spectra show shifts due to the presence of certain anions that participate in complex formation.[123] The photoisomerism of mercury dithizonate has already been observed and thoroughly investigated,[3,35,42] while Briscoe and Cooksey had reported on formation and absorption spectra of such species as $ClHg(HDz)$;[124] adsorption and the effort of complexing on the distribution coefficient could explain other of these observations.

After extracting 99.1 to 99.8% of mercury as $Hg(HDz)_2$ from waste waters containing 10^{-3} to $10^{-1}\ \mu g\ \ell^{-1}$, the complex is adsorbed on carbon and then volatilized at 400 to 500°C and mercury vapor determined spectroscopically at 2536 Å.[125] On the other hand, while mercury has been extracted directly from seawater[126] or lake waters before transforming to the vapor state for measurement,[127] its separation from high-purity silver was achieved by coprecipitation with silver iodide in the presence of EDTA, stripping with sodium thiocyanate, and spectrophotometry as $Hg(HDz)_2$.[128] Massa extracted mercury from 1-g samples of opthalmic ointment and chromatographed the dithizonate on a silica gel plate and determined the amount densitometrically.[129]

After dry ashing biological samples in oxygen, Kosta and Byrne concentrated mercury vapor on selenium-impregnated paper after removing interfering substances such as chlorine or bromine with silver wool. After activation to mercury-203 and adding carrier mercury, the whole was extracted with dithizone for scintillation counting.[129,130] The extraction of $Hg(HDz)_2$ and its transference to ClHg(HDz) forms the basis of an automated analysis by substoichiometric radioisotope dilution.

When trace metals are present and large volumes of, e.g., waste waters have to be handled to secure adequate preconcentration, liquid-liquid extraction presents certain practical disadvantages that are overcome if solid absorbents are used in column form. Tahara was able to reduce the mercury content of sodium chloride solution initially containing 10 to 30 ppm Hg and 10 to 20 ppm Cu to less than 1 ppm Hg by adjusting to pH 4 to 6 and passage down a resin column loaded with dithizone.[132] Better than 96% recovery from seawater containing 0.05 to 1.0 ppm Hg can be achieved with a column of polysyrene beads coated with dithizone gels,[133] and separation from Fe, Pb, Zn, Cd, and Cu(II) can be effected by working at pH $\sim$1 with EDTA as a masking agent leading to enrichment of mercury(II) down to the parts per billion level.[134] If the column is prepared by soaking in 0.07% H_2Dz in chlorobenzene and then this is transformed into the zinc complex, $Zn(HDz)_2$, the rose colored beads go orange as mercury(II) ions patss through, the length of the orange zone being proportional to the concentration of mercury.[16,155] Much the same principle is involved in the determination of mercury. ($\leq$0.2 μg) by displacing radioactive zinc-65 from $Zn^{65}(HDz)_2$,[135] and small amounts of mercury in pesticides for seed dressing can be determined after wet-ashing with $KMnO_4$-H_2SO_4 by immersing a strip of paper impregnated with Ag(HDz); the area of color change is proportional to the mercury(II).[136]

The extraction of a very large number of alkyl- and aryl-mercury(II) dithizonates has been reported,[36,137] and Kiwan and Fouda have proposed a spectrophotometric method for the simultaneous measurement of organomercury(II) and inorganic mercury(II) ions.[138]

This problem of the separation and/or determination of inorganic and organic mercury compounds has promoted much interest. Selective separation of ionic Hg^{2+} from RHg^+ on soda-calcium glass microbeads has been reported.[139] Tokeshita et al. separated the dithizonates by reversed phase TLC,[63] but other workers have preferred wet oxidation as a preliminary to dithizone extraction.[140-142] Whereas diaryl mercury compounds, Ar_2Hg, are said not to react with dithizone, and $ArHg^+$ gives the primary dithizonate ArHg(HDz), there is evidence that the carbon-mercury bond is broken in the presence of a large excess of dithizone;[137,143] if this is a general phenomenon it has implications both in quantitative analysis and in separational problems. Other chromatographic separations are quite numerous.[51,54-56,60,65,128] After a preliminary extraction as $Hg(HDz)_2$, mercury can be determined polarographically.[144] Tomcsanyi has recently used a 5×10^{-3} *M* solution of dithizone in acetonitrile for the amperometric titration of mercury(II) (2-50 $\times 10^{-6}$ *M*) at the dropping mercury electrode or with a rotating carbon paste electrode. Precision of ±5% is claimed for traces of mercury in aluminum, gallium, and zinc.[145]

A completely novel observation is the formation of a water-soluble complex (λ_{max} = 555 nm; ε_{max} = 8360 $m^2\ mol^{-1}$) formed by mercury and dithizone at pH 12.9 in the presence of *N*-cetylpyridinium chloride.[146] This clearly merits further study.

N. Nickel

The use of dithizone for the determination of nickel has never been very popular,[12] partly from lack of selectivity, partly from the slow rate of extraction, and partly owing to the absence of marked features in its absorption spectrum. The fact that addition of pyridine enhanced the rate of extraction and induced a change in absorption spectrum[81] led Math and Frieser to investigate adduct formation between $Ni(HDz)_2$ and pyridine bases,[147] and to elaborate a method in which nickel is determined as $Ni(HDz)_2(phenan)$ (phenan = 1,10-phenanthroline), in which the 4-banded spectrum of nickel dithizonate has been replaced by a single band at 520 to 535 nm with ε_{max} = 4910 m² mol⁻¹.[148]

Dithizone has been used in chromatographic separations[54,60,65,67] and to isolate the element prior to determination by ASS.[80,86,89]

O. Palladium

There have been few uses made of the palladium dithizonate complex in analytical chemistry, though it finds application in the substoichiometric determination of 3 ng in platinum, W-1, PCC-1, and biological materials,.[149,150] Chromatographic separations have been described,[54,60] and Eckelman et al. report that, besides assisting the nebulization of gold, mutual interferences of gold, platinum, and palladium in AAS are eliminated by using dithizone.[151]

Minczewski et al. have reexamined the composition of complexes formed between dithizone and palladium under various conditions. The green primary complex $Pd(HDz)_2$ extracted by H_2Dz/CCl_4 or $CHCl_3$ from acidic solutions can be back-extracted by ammonia or NaOH to give a color ascribed to $[Pd(HDz)_2(OH)_2]^{2-}$, and the red secondary dithizonate, PdDz, formed from excess palladium, gives water-soluble pink $[PdDz(NH_3)_2(OH)_2]^{2-}$ when in contact with ammonia.[152]

P. Platinum

There has been little activity since 1969; apart from reported separations by chromatography,[60] the element has been determined by extraction-spectrophotometry,[153] by AAS,[151] and by substoichiometry.[154]

Q. Polonium

Little use seems to have been made of the formation of the extractable red $Po(HDz)_2$[12] though Sebesta exploited this in a chromatographic separation of a radioactive mixture with lead and bismuth.[56]

R. Selenium

Dithizone was first employed for the determination of traces of selenium by Mabuchi and Nakahara in 1963,[156] and later by Shcherbov et al. in 1967.[157] In 1970 a spectrophotometric determination of selenium using dithizone was applied to the determination of impurities in high-purity tellurium.[158]

In their important studies of ligand exchange in organic media Stary and Ruzicka prepared selenium dithizonate by treating selenium(IV) in 5 *M* HCl with excess dithizone and removing unreacted reagent by shaking with dilute ammonia.[159] The 1:4 stoichiometry was established spectrophotometrically *inter alia* by the exchange reactions

$$Se(HDz)_4 + 4HDDC \rightarrow Se(DDC)_4 + 4H_2Dz \qquad (18)$$

$$Se(HDz)_4 + 2Cd(DDC)_2 \rightarrow Se(DDC)_4 + 2Cd(HDz)_2 \qquad (19)$$

although attempts to measure the equilibrium constant of Equation 18 "did not give reproducible results".

The quite unique stoichiometry (1:4), the unusually low molar extinction coefficient (ε_{max} = 7000 m^2 mol^{-1}) for a complex containing four dithizone residues, comments made previously by Mabuchi and Nakahara who had reported very low percentage extractions when using selenium-75 as tracer,[156] and the reported absorption band of the yellow selenium dithizonate (λ_{max} ~410 to 420 nm), which was virtually identical with that of the yellow disulfide (16) obtained by oxidizing dithizone with iodine (and other mild oxidants), led Ramakrisha and Irving to suggest that the alleged selenium dithizonate was only an oxidation product of dithizone so that the reaction between the known oxidant Se(IV) in acidic media should be formulated thus:[160]

$$SeO_2 + 4H_2Dz\,(org) \rightarrow Se^0 + 2(HDz)_2\,(org) + 2H_2O \qquad (20)$$

rather than

$$SeO_2 + 4H_2Dz\,(org) \rightarrow Se(HDz)_4\,(org) + 2H_2O \qquad (21)$$

Consistent with this hypothesis it was found that the yellow product obtained from dithizone and Se(IV) behaved spectrophotometrically in the same manner as the known disulfide (16); in particular it spontaneously disproportionated into the mesoionic compound (17) and dithizone (6) so that the green color and spectrum of this reagent appeared (slowly in CCl_4, much faster in $CHCl_3$); it was immediately reduced to dithizone by adding HDDC.[160] Some solid selenium was formed, but much remained dissolved (or in colloidal solution) in the organic solvent.

On the other hand, by using tracer selenium-75, Stary et al. showed that selenium was quantitatively extracted by dithizone from 1 to 12 *M* HCl provided $[H_2Dz] > 5 \times 10^{-5}$ *M*, and slowly and to a limited extent from 5 *M* HCl even in the absence of dithizone. The plot of log D against $\log[H_2Dz]_{org}$ had a slope of 4 in 1 *M* HCl, which appeared to confirm Equation 18 although it would, of course, be equally consistent with 20 or 22; it seems that all the selenium remained in the organic phase, not an improbability since $[Se] < 10^{-7}$ *M*.

More decisive experiments were comparisons of the behavior during TLC on silica gel of (1) a mixture of elementary selenium-75 and the disulfide (16), (2) the disulfide (16), (3) ^{75}Se-dithizonate, (4) a mixture of elementary ^{75}Se, ^{75}Se-dithizonate, and the disulfide (16), and (5) elementary ^{75}Se alone. The R_f value for selenium dithizonate and the disulfide were obtained from the position of the yellow bands and the location of selenium-75 was detected by autoradiography.[161,162] The results clearly disprove Equation 20, for mixture (1) behaved quite differently from (3). However two colored zones appeared with mixture (3) and this suggests the possibility of the reaction

$$SeO_2 + 4(H_2Dz)\,(org) \rightarrow Se(HDz)_2\,(org) + (HDz)_2\,(org) + 2H_2O \quad (22)$$

where both selenium(II) dithizonate and the disulfide (16) are formed and co-extracted into an organic phase, both having closely similar absorption spectra. This explanation would then correspond to the behavior of tellurium(IV) (q.v.) and that proposed by Busev for the extraction of selenium by diethyldithiophosphoric acid or 2-mercaptobenzimidazole.[162]

The instability of selenium dithizonate, (i.e., the material produced by the reaction of Se(IV) and dithizone and probably due to gradual disproportionation of accompanying disulfide (16) has been commented upon by several workers, and although Boerig and Heigener concentrated selenium by extracting biomaterials with H_2Dz/CCl_4, they preferred to destroy the dithizone ligand and determine residual selenium with 3,3'-diaminobenzidine.[163] Iordanov and Daskalova noted that the oxidation of dithizone by nitric acid gave a product with the same electronic spectrum as selenium(IV) dithizonate and suggested that this complex did not exist under the conditions of measurement.[164] Other workers, however, determined selenium in platinum metals by the dithizone method with no apparent difficulties.[165]

In a recent paper Russian workers utilize the "unstable yellow color" formed when SeO_2 reacts with dithizone in an indirect way, for after stripping excess dithizone with dilute ammonia they reduce the yellow SeO_2-H_2Dz reaction products and measure the stable resulting green color of the dithizone so formed. Conditions for maximum absorbance at 620 nm (using $SnCl_2$-HCl as reductant) are discussed in detail and 0.3 to 10 μg Se could be determined with a relative standard deviation $\leqslant 0.3$.[166] In analyses of mixed raw materials or products of processing,[166] 50, 10, and 10 g/ton of silver, gold, or tellurium, respectively, could be tolerated.

S. Silver

The classical dithizone methods for silver were well tried and proven by 1972,[12] and Wichrowska noted that it was more sensitive than rhodanine (by going down to 0.002 to 0.1 ppm.), but needed much equipment.[167] Spectrophotometry of Ag(HDz) at 490 nm was used to determine silver concentrations in the sea around Monaco after preconcentration on PbS,[168] while Marzenko and Podsiadlo determined silver impurities in thin layer Cd-Hg-Tl semiconductors in an elaborate procedure in which silver and mercury were first estimated together at 462 nm and silver alone after suitable masking.[15] Mascovschi details two methods for spectrophotometric determinations carried out in a homogeneous aqueous-acetone system.[169] Dithizone has also been used in activation analysis for the preliminary separation of silver,[170,171] and in a special new procedure for substoichiometry, which was illustrated by the separation of silver and copper from cobalt. The theory of this new method has been given in detail.[172]

In place of an extractive titration with a spectrophotometric endpoint, Russian workers have shown that microgram amounts of silver, mercury(I), mercury(II), cadmium, or palladium can be titrated with $H_2Dz/CHCl_3$ or C_6H_6 with an amperometric endpoint with no lower sensitivity (error 0.1 to 11.3%).[173] Some chromatographic separations have been reported[51,56,58,60] and filter paper impregnated with Ag(HDz) has been used for the semiquantitative determination of mercury.[136]

T. Tellurium

The definitive work by Sandell and Marhenke in 1967 on the extraction of Te(IV) by dithizone does not appear to have been followed up or used much in recent years.[12] Indeed the oxidation product of dithizone produced during the determination as Te(IV) is reduced to $Te(HDz)_2$ has not been formally identified.

U. Thallium

Although the extraction of the red Te(HDz) has long been established,[12] dithizone has been used almost exclusively as an extracting agent; photometric finishes have rarely used the dithizonate, preferring, e.g., rhodamine B as the determining reagent with a spectrophotometric or fluorimetric finish.[74] Thallium(III) has never been successfully determined with dithizone, the reason being that this reaction is very complicated since the stoichiometry and the nature of the products is dependent on the relative concentration of reactants, the acidity, the order of mixing, and also on the time of equilibriation.[29] In this respect the powerfully oxidizing Tl^{3+} shows resemblances to Au(III) (q.v.).

V. Thorium

Thorium is said to form a 1:2 complex with dithizone that could be used for the quantitative determination of this element.[175] The fact that beryllium — not previously reported as reacting with dithizone — is among many elements, (e.g., Al, Zn, Mg, Ca, etc.) that are noted as interfering suggests that this interesting observation merits further work.

W. Tin

Up to 1957 most interest had been centered on the determination of tin (II).[12] In that year Aldridge and Cremer showed that Et_3Sn^+ salts gave a yellow extractable complex with dithizone and Et_2Sn^{2+} an orange complex, while $SnCl_4$ and Et_4Sn did not react.[3,12] With the increasing use of orango-tin compounds in wood preservatives and as stabilizers for PVC, interest in their separation and analysis has increased.[51,55,176] The observation by Skeel and Bricker (1961) that λ_{max} for the extractable dithizone complex of Bu_2SnCl_2 appeared to depend on the pH, the concentration, and the composition of the buffer system employed was explained later by Kamara and Takei, who showed that whereas a 1:1 complex $Bu_2Sn(HDz)X$ (λ_{max} = 499 nm, where X = $CH_2Cl.COO^-$) was extracted by a phosphate buffer, and a mixture of the two (X = $HCOO^-$ or CH_3COO^-) from a formate or acetate buffer.[177] All the mixed complexes had their maximum absorption in the range 479 to 499 nm with ε_{max} 3660 to 3890 m^2 mol^{-1} Complexes of Pr_3Sn^+ behaved similarly.

Mikami and Takei made a comparable study of carboxylate complexes of Pr_3Sn^+ and found that the distribution ratio $D = [Pr_3Sn^{IV}]_{org}/([Pr_3Sn^+] + [Pr_3SnA])$ increased in the order 6.9, 7, 9, 68, and 2500 as HA changed from acetic, formic, chloroacetic, to dichloroacetic acid. The use of dithizone as a spray reagent for developing colors after TLC of organotin complexes has already been mentioned.[62] Herold and Droege separated lower alkyls present as impurities in octyltin(IV) complexes by TLC and carried out a spectroscopic determination with dithizone.[179] Vrestal and Havir prefer to extract compounds of R_3Sn^+ from alkaline EDTA or 0.02 *M* sodium cyanide into chlorobenzene, and then carry out a photometric titration with 10^{-4} *M* dithizone. The sensitivity is 0.003 mg for $Bu_3Sn\text{-}O\text{-}SnBu_3$, and other alkyl tin compounds; organic acids and cations that normally react with dithizone do not interfere under these circumstances.[180] With complex mixtures Freitag and Bock first extract $(C_6H_5)_3Sn\text{-}O\text{-}Sn(C_6H_5)_3$ with chloroform at pH 8.5, then $(C_6H_5)_2Sn^{2+}$ compounds with dithizone/$CHCl_3$ at pH 8.5, then compounds of $C_6H_5Sn^{3+}$ with tropolone, and finally Sn(IV) with NaDDTC/$CHCl_3$ at pH 4.[181]

Separations by TLC of mixed organotin salts, ($(C_6H_5)_nSnCl_{4-n}$, $n = 0$ to 3) have been described using a variety of physical determinations for quantitative work.[181] Zaidi (1973) has reported the formation of a stable complex $SnBr_4(H_2Dz)_2$ in chloroform with ε = 285 m^2 mol^{-1} at 510 nm.[182]

X. Uranium

A 1:2 complex of uranium(VI) and dithizone has recently been reported.[175]

Y. Zinc

The determination of zinc continues to provide problems for the analytical chemist. For samples of rubber after wet ashing with a mixture of concentrated $HNO_3\text{-}H_2SO_4$

the addition of dithizone produces a color that can be compared with those from dithizone and known amounts of zinc in the range 0.16 to 0.59 ppm.[183]

Tikhamirova prefers thiosulfate to thiourea for masking Cu(II) and fluoride ions for Fe(III) in an extractive photometric method,[184] and details of a monocolor spectrophotometric method for Pb, Zn, and Cd have been reported.[48]

Spectrophotometric methods for the determination of zinc in sedimentary rocks,[185] in biological specimens,[186] and in serum,[187] present no particularly novel features, but in a comparative study of methods for determining zinc in water by colorimetric methods Sikorowka and Wichrowska conclude that the two-color method is the best using $CHCl_3$ for 1 to 5 mg ℓ^{-1} and CCl_4 for 0 to 0.5 mg ℓ^{-1}.[188]

The role of zinc traces in soils has excited considerable recent interest. The absorption and release of zinc from systems containing clay has been studied with zinc-65 through a dithizone method, and the dithizone determinations provided the best correlation between extractable zinc and zinc taken up by tomato plants.[189] Distinction between free zinc in sea water and the total extractable after persulfate oxidation has been discussed,[190] and Fukai and Huynh-Ngoc conclude that total zinc can only be determined after strong oxidation, whereas recoveries by dithizone extraction at pH 7 are comparable to anodic stripping voltammetry at pH 8 — and correspond to ionic and labile forms of zinc, while chelating resins or ferric hydroxide include some zinc combined as colloids and as organic compounds.[191] Rastogi and Raj have examined a number of possible extractants for determining zinc in black soils for growing wheat in India,[192] and Elsokkhary favors EDTA to dithizone for various alluvial and calcareous soils in Egypt.[193] Roberts et al. describe the simultaneous extraction and determination of cadmium and zinc in soil extracts,[78] while Florence and Batley review the determination of zinc and other elements (Cd, Cu, and Pb) present in various chemical forms in natural waters.[77]

Atomic absorption spectroscopy has been used for the determination of zinc and copper in high-purity tungsten and molybdenum,[80] and for zinc, cobalt, copper, and nickel in rocks and sediments.[86] Trace determinations by isotope dilution[194] and by substoichiometry have been described.[195,196] In the latter case the final stage involved a substoichiometric amount of 8-quinolinol-5-sulfonic acid, interfering metals such as iron(III), copper(II), cobalt, cadmium, mercury(II), and nickel having previously been removed with 0.001% H_2Dz/CCl_4 at pH 7. In addition to many other chromatographic separations,[16,51,53-8,60,64-67] sub-ppm levels of zinc(II) can be determined by passing a solution at pH 6.2 down a column of dithizone gel beads; the color changes from green to pink and the length of the pink zone is proportional to the amount of zinc in solution. Interference from Ag, Bi, Co, Cu, Fe, Hg, and Pb was prevented by combined use of $Na_2S_2O_3$, 2,2′-bipyridyl, hydroxylamine hydrochloride, *N,N*-bis(β-hydroxyethyl)dithiocarbamide and β-dithiocarbaminopropionic acid, and recoveries were quantitative.[16]

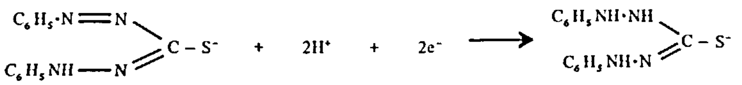
Perrin has shown how a digital computer can be applied through the program MINICOMICS to studies of the selective extraction of zinc by dithizone,[197] and the effect of auxiliary complexing agents on the rate of extracting zinc (and nickel(II)) by dithizone has been studied by Freiser et al.[198]

V. DITHIZONE AND ELECTROCHEMISTRY

A. Basic Studies

Supplementing earlier work by Kemula, Najdeker, and Kublik (1963), Yamashita made a broad study of dithizone and its chelates with Cu(II) and Hg(II) using DC, AC, and cyclic voltammetry with the hanging drop, and dropping mercury and glassy carbon electrodes. Well-defined reduction waves for $Hg(HDz)_2$ and $Cu(HDz)_2$ were observed at −0.32 and −0.41 V and both underwent irreversible six-electron reduction to H_4Dz (diphenylthiocarbazide).[199]

Sharma et al. reported a single reduction wave for dithizone in acidic 10^{-4} *M* solutions, but at pH <9.0 two reduction waves were distinguished and a third appeared at pH >9, possibly a radical that could combine with itself or added polyvalent cation. In unbuffered solutions at pH 8.5 there were two waves, one ascribable to the reduction of H^+ dissociated from the dithionate ion.[200] Tomcsanyi's studies led to the identification of one oxidation and two reduction waves at pH >7. The first well-defined reduction wave has a maximum of the first kind depending on $[H_2Dz]$ and the composition of the supporting electrolyte. The second wave is reversible and diffusion controlled in 1 *M* NaOH-0.2 *M* Na_2SO_4 − 20% ethanol and in 1 *M* NH_4OH — 1 *M* NH_4Cl — 20% ethanol; $E_{1/2}$ is a linear function of pH from 2 to 14 with a slope of 59.6 mV/pH and the number of protons involved equals the number of electrons, $n = z$. These results point to the azo → hydrazo reduction



$$C_6H_5{\cdot}N{=}N{-}C(S^-){=}N{-}NH{\cdot}C_6H_5 + 2H^+ + 2e^- \longrightarrow C_6H_5NH{\cdot}NH{-}C(S^-){=}N{\cdot}NH{\cdot}C_6H_5$$

HDz^- (13) H_3Dz^- (19)

Since the limiting current is proportional to $[H_2Dz]$ in the range 10^{-3} *M* to 10^{-5} *M*, dithizone can be determined polarographically with a relative error ≤±3% in 1 *M* NaOH — 0.2 *M* Na_2SO_4 — 20% ethanol.[201]

In a second paper, Tomcsanyi observed the changes in spectrum that accompany the controlled-potential electrolysis of dithizone on a macroscale.[202] The two-electron reduction to a hydrazo compound (2) or (5) was confirmed, and it was found that during autoxidation of dithizonate ions, HDz^- (13), in alkaline solution by atmospheric oxygen one product is reduced in a two-electron step; this new reduction wave at −1.25 V disappears in a completely oxidized solution. These changes correspond to the reactions

$$HDS{-}SDH + 2e^- \longrightarrow 2HDS^- \qquad (23)$$

or, in the nomenclature used above, to the reduction of 1 mol of the disulfide (16) to 2 mol of the dithizonate anion HDz^- (13). The mesoionic tetrazolium derivative (17) was reduced to the dithizonate ion also, and since $E_{1/2}$ was a linear function of pH with a slope of 29 mV/pH over the range pH 9 to 14 this change must correspond to

$$\underset{(17)}{\text{mesoionic compound}} + 2H^+ + 2e^- \rightarrow \underset{(13)}{HDz^-}$$

Further reduction takes place at the −N=N− bond. These results completely support the author's own account (v.s.) of the deterioration of solutions of dithizone.[40] Electro-oxidation of dithizone at a carbon electrode leads to an insoluble layer (possibly of disulfide) and the limiting current is proportional to $[H_2Dz]$.[202]

Kambara and Hara studied the AC polarography of dithizone and noted very sharp peaks in aqueous-alkaline solution where DC steps may be ill-defined.[144] The peak at about −0,4 V vs. mercury pool electrode is unaffected by temperature change for pH 12.4 to 12.9 and at 25 ±0.1°C and pH 12.5 the peak height is an almost linear function of [H_2Dz] up to 3×10^{-5} *M*. This lends itself to an indirect microdetermination of mercury(II). After preliminary extraction of $Hg(HDz)_2$ from 0.5 *N* H_2SO_4 into benzene and removal of excess H_2Dz with 0.15 *N* NH_4OH the mercury is stripped with a potassium iodide — potassium hydrogen phthalate reversion mixture and the (two) equivalents of dithizone that remain in the organic phase are then stripped with N-NaOH and determined polarographically with Na_2SO_4 as the supporting electrolyte.[144]

B. Applications

1. Polarographic Finishes

Conventional polarography can be used for many metals and Bi, Cd, Co, Cu, Ni, Pb, and Zn are among those that have been determined in a wide range of inorganic and biological samples.[12,108,144,203] Karbainov and Stromberg studied the polarography of $Cd(HDz)_2$ and $Pb(HDz)_2$ in a monophase of chloroform and methanol.[107] Preconcentration and separation from interfering elements must often be achieved by a preliminary extraction with dithizone, although excess reagent and organic solvent must normally be removed before polarography.[144,203] Fano et al. extract metals with 25 m*M* $H_2Dz/CHCl_3$ or C_6H_6 and then add $AgNO_3$ dissolved in methanol until all excess dithizone is bound in 2:1 excess. The solution is then made up with methanol and polarographed with 2 *M* $NaNO_3$ as supporting electrolyte with a solvent mixture ratio CH_3OH to C_6H_6 = 7:1 for the concentration range 0.025 to 0.25 ppm.[108]

2. Amperometric Analysis

Tomacsanyi gave special attention to the conditions under which dithizone and mercury(II) ions underwent reduction at the dropping mercury electrode.[145] This led to a rapid procedure in which 2 to 15 × 10^{-6} *M* Hg^{2+} could be determined amperometrically in 15 min with a relative error <±5%. Cu(II), Hg(II), and Zn(II) in the range 2 to 20 × 10^{-6} *M* could be determined with a reproducibility better than 5% by amperometric titration at a rotating carbon paste electrode in 1 *M* H_2SO_4, 0.2 *M* sodium acetate, and 0.02 *M* HCl, respectively. Dithizone was also used to determine traces of mercury(II) (to ±5%) in 10^{-3} *M* gallium, 10^{-5} *M* zinc, and 10^{-2} *M* aluminum.[145] The procedure has been applied to microgram quantities of cadmium, silver, mercury(I), and (II), and palladium using $H_2Dz/CHCl_3$ or C_6H_6 as titrant.[173]

3. Stripping Voltammetry

Cathodic stripping can be employed after a preconcentration stage by liquid-liquid extraction, or after anodic preconcentration as a sparingly soluble complex of mercury(II). Another possibility is to prepare a complex with excess of a selected metal ion followed by determination of remaining metal by anodic stripping voltammetry. Stromberg et al. appear to have been the first to use this for the determination of ultratrace impurities.[204] Fano et al. determined cadmium, lead, and zinc by direct stripping voltammetry,[108] and Vydra and Nghi used the technique to determine metals in a nonaqueous medium with a mercury film prepared *in situ* on a rotating glassy carbon disc electrode.[109] After a preliminary extraction with $H_2Dz/CHCl_3$ the organic phase was separated and excess of $HgCl_2$ added to displace the lead from the $Pb(HDz)_2$ and to complex excess dithizone and to form the mercury film *in situ*. With lithium chloride as a supporting electrolyte at −0.9 to −1.0 V, 5 × 10^{-7} *M* lead could be determined with 3 to 4% error after separation from millimolar amounts of Ag^+, Bi^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, and Sn^{4+}.

4. Coulometric Titrimetry

A procedure for the determination of platinum (0.02 to 5 mg) has been worked out by Gruetzner and Lehmann.[205] After extraction with $H_2Dz/CHCl_3$ in the presence of tin(II) chloride, silver nitrate is added to bind excess reagent. The organic phase is diluted with ethanol and heated with sodium bromide and the platinum dithizonate is titrated with anodically generated bromine. Silver and iridium do not interfere.

VI. SOME SPECIAL APPLICATIONS OF DITHIZONE

A. Preconcentration

The analytical problems involved in the determination of a particular component in a complex matrix, especially when this desired constituent is present in trace amounts, may be loosely identified as (1) the preliminary treatment of the sample, (2) preconcentration and separation of the required constituent(s), and (3) the final determination. These stages are to a great extent interdependent. For example, although the degree of preconcentration must depend on the initial concentration in the bulk sample, it will be determined by the minimum amount of the isolated constituent needed to carry out the final determination with the accuracy and precision acceptable for the purpose in hand. The extent to which potentially interfering substances must be separated will depend on the characteristic features of the final determination procedure (the "finish") and, of course, on the nature of these interferences. Thus, when determining trace metals, mutual interferences will normally be greater in emission spectrography than in atomic absorption; on the other hand the former technique lends itself to simultaneous multicomponent analyses. One spectrophotometric finish may be more selective than another. Neutron activation procedures can (usually) eliminate matrix effects and the need for preconcentration and the problems of blanks, although postirradiation separations now assume a much greater significance.

Dithizone is almost unique in the extent to which it can be participate in both preconcentration and separation stages, and in various finishes, not only those involving spectrophotometry as we have seen above. Examples of its ability to preconcentrate one or more of the dithizone metals by liquid-liquid extraction abound in the above pages. Examples are bismuth,[87] cadmium,[214,215] cobalt,[86] copper,[86,87,214] gold,[216] indium,[215] lead,[43,214,215] mercury,[216] nickel,[86] silver,[171,214,215] thallium,[174] and zinc;[86,214] this is by no means a comprehensive listing. Lel'chuk et al. made use of the nonspecific behavior of dithizone in a method for the determination of total heavy metals in demineralized water.[206] Here 10 cm^3 of the sample and 10 cm^3 of triply-distilled water are suitably buffered, and each is mixed with 1 cm^3 of H_2Dz/CCl_4 and then titrated with standard $ZnCl_2$ to a color match. Total metal concentrations >0.5 μg ℓ^{-1} are determined to ±10 to 20%.

The use of an absorbent column facilitates the extraction and concentration of constituents from dilute solution. For removal purposes, dithizone on a resin column has been used to reduce the concentration in brines below 1 ppm.[132] Ito et al. have patented a column of active carbon containing 2% of dithizone, which will take up 10 g of copper per liter of absorbent and can be regenerated with 10% K_2S,[207] and a chelating resin coupling product of diazotized cellulose and dithizone or 8-quinolinol will give enrichment factors of 42, 2200, and 27,000 for the mercury, copper, and gold, respectively, from 10- to 20-ℓ samples of seawater; the metals can be eluted and the columns regenerated with hydrochloric acid and ammonium chloride.[208]

Chromatographic columns using dithizone supported on alumina, cellulose, silica gel, or other materials have been used to collect and preconcentrate metals such as gallium, indium, mercury, and zinc,[6,63-66,80,134] but more recent development has been the use of plasticized open-cell polyurethane foams. Braun and Farag have investigated the influence of different plasticizers, the pH, the concentration of dithizone, and other factors on the velocity and completeness with which silver, mercury, zinc, and lead are taken up by dithizone foams or by foams treated with zinc dithizonate.[209,210] Chow and Buksak applied this technique to the preconcentration and separation of Hg^{2+} and CH_3Hg^+, the former being taken up at pH 5 to 10, the latter effectively quantitatively at pH 1.2. Conditions for washing and regenerating the column are reported.[211] Hydrophobic gel particles containing dithizone have been shown to collect mercury(II) from solutions containing as little as 0.72 to 72 ppm, and the metal can then be stripped with aqueous thiosulphate.[212] The proportionality between the amount of metal absorbed and the length of the zone in a dithizone column where the color has changed from green to pink (or orange) has been used for the determination of zinc,[16] or mercury.[155,213] With a 3 × 100 mm column, each 1 cm length of orange zone corresponds to 0.1 ppm mercury(II) per 100 cm^3 water passed.[155]

B. Atomic Absorption Spectrophotometry

Although a preliminary extraction with dithizone simplifies many emission spectrographic procedures, since this eliminates the multi-line spectra due to iron etc.,[3,217] this technique is still more effective in collecting a range of elements for X-ray fluorescence and especially for atomic absorption or atomic fluorescence spectroscopy.

After preliminary extraction with dithizone, AAS has been used for the determination of copper in pure WO_3 or MoO_3,[80] rocks and sediments,[86] nickel and cobalt salts,[89] foodstuffs[90] and organic solvents;[214] cadmium in soil extracts,[78] organic solvents,[214] in zirconium and its alloys,[220] and in natural waters;[215] cobalt in rocks and minerals;[86] gold;[151] indium in rain and stream waters;[215] lead in steels,[43] foodstuffs,[90] biological materials,[101] plant and animal materials,[102] air,[103] blood,[104] petroleum products,[106] organolead salts,[114] organic solvents,[214] and natural waters;[215] nickel in rock materials;[86] palladium and platinum;[151] silver in foodstuffs,[90] organic solvents,[214] or natural waters;[215] and zinc in soil extracts,[78] pure MoO_3 and WO_3,[80] rocks and sediments,[86] foodstuffs,[90] and organic solvents.[214]

There is no objection to introducing the organic phase from a dithizone extraction in CCl_4 or $CHCl_3$ directly into the flame, provided there is adequate ventilation, but reproducibility is often improved by evaporating off these solvents and taking up the residue in water. Removal of solvent is, of course, a prerequisite when using a carbon rod furnace with its enhanced sensitivity.[106] Since acetone has been shown to be the solvent of choice for obtaining optimal detection limits in flame spectroscopy, Matkovich and Christian have recently studied the conditions under which a variety of metal dithizonates can be extracted into acetone, for this can be salted out by adding calcium chloride or 65% sucrose to the aqueous phase.[44] Ethyl propionate has previously been recommended.[218]

Oelschläger and Frenkel[102] emphasize the fact that significant errors in direct AAS of lead in plant and animal materials can be reduced by preliminary extraction with $H_2Dz/CHCl_3$, and Ekelmans et al. find that mutal interferences in the determination of mixtures of gold, palladium, and platinum when nebulizing aqueous solutions in an air-acetylene flame are reduced by complex formation with dithizone, which also appears to facilitate the atomization of gold.[151] A comparative study of AAS and the wet chemistry (dithizone) method for the determination of atmospheric lead showed no statistically significant difference at the 0.05 level.[103]

C. Activation Analysis and Substoichiometry

The basic principles of activation analysis are well known. The sample containing the unknown amount, x, of the element to be determined is irradiated simultaneously with a known and comparable amount, m, of the pure element under identical conditions. After adding a relatively large amount of carrier element to each, a radiochemically pure sample of a suitable compound of the desired element is isolated in each case. If the specific activities are A_1 for the sample, and A_2 for the standard, $x = mA_1/A_2$.

Clearly dithizone will prove invaluable in the post-irradiation stages either for the extraction of undesired elements or for the concentration and separation of the desired one. There remains the difficulty of computing the *specific* activity, for this requires a knowledge of the chemical yield, which may be low and certainly not the same for the standard and sample. In 1961 Růžička and Starý developed a new principle by which the same amount of dithizone was employed to extract the irradiated element in both sample and standard, but in an amount insufficient to combine with all the irradiated element in either case. Since the amount of primary dithizonate extracted will necessarily be the same for both sample and standard, the measured activities will be a direct measure of the specific activities and hence of the relative amounts of element present in the sample and in the standard.[8-11] The procedure has been refined and extended in various ways over the years and activation analysis, generally employing this principle of substoichiometry has been used for many elements,[3,12] and during the past ten years for the determination of cadmium in biological tissues,[29] in the presence of Ag, Bi, Co, Cu, Hg, Mn, Ni, Pb, and Tl,[79] and in gallium arsenide together with Cu, Mn, and Zn.[211] Copper has been determined in mussels together with iron and zinc,[67] and in gallium arsenide;[221] gold in platinum, and together with nickel and silver in gallium arsenide;[170] manganese and nickel in gallium arsenide;[170,221] mercury in laboratory chemicals,[134] and in biological samples;[129] palladium in platinum, W-1, PCC-1, and biological material;[149] platinum in rocks[154] silver in rocks[171] and in gallium arsenide;[170] zinc in mussels[67] and in seawater.[195] Indium and tin have been determined by activation analysis using replacement stoichiometry.[222]

An interesting point arises in the determination of traces of gold in platinum, for the nuclear reaction $^{196}\mathrm{Pt}(n, \gamma)^{197}\mathrm{Pt} \rightarrow {}^{197}\mathrm{Au}$ gives rise to spurious gold so that the overestimated value of gold would increase (1) with the neutron flux, (2) with the time of irradiation, and (3) with decreasing proportions of gold in platinum. The problem is overcome by a preliminary oxidation of a solution in concentrated HCl to give Pt(IV) and Au(III). On passage through a column of dithizone adsorbed on resin, only the latter is retained as its dithizonate and platinum is washed out. The resin column (in a tube of plastic) is sealed off and irradiated in the usual way.[223] Here separation of the interfering element takes place before irradiation.

Some care must be taken in adapting these procedures of substoichiometry to automation.[131] For example the formula $Hg(HDz)_2$ for mercury(II) dithizonate would seem to ensure a constant stoichiometry 1 mol $H_2Dz \equiv \frac{1}{2}$ mol Hg^{2+}. However in the presence of e.g., chloride ions in significant concentration, the compound HgCl(HDz) is extracted and the ratio would be 1 mol H Dz $\equiv$ 1 mol Hg^{2+}.[124] It is thus not sufficient merely to employ a substoichiometric amount of the ligand, but to ensure that in replicate analysis all other parameters that could influence the extraction are unchanged.

Instead of liquid-liquid extraction with a substoichiometric amount of a solution of reagent, Akaiwa et al. removed zinc from other metals with an anion-exchanger loaded with a substoichiometric amount of 8-quinolinol-5-sulfonic acid. Interfering elements (iron(III), copper(II), cadmium, cobalt, nickel, and mercury(II)) were removed with 0.001% H_2Dz/CCl_4 at pH 7. The principle of substoichiometry for separating many elements by extracting their metal chelates has been thoroughly discussed by Elek and co-workers,[172,224] and by Starý and Lamm.[234]

D. Ion-Selective Electrodes

1. General Theory

One of the most fruitful developments in analytical chemistry during the past decade has been the introduction of ion-selective electrodes following on the discovery of the lanthanum fluoride solid-state electrode by Frant and Ross in 1966. The *liquid-state electrode* comprises a thin film of organic liquid absorbed on the surface of a conducting material such as porous organophilic graphite: a stainless steel contact to the inner surface of the graphite plug (which is contained in a plastic sheath) obviates the need for an inner reference solution.[225]

If the film comprising the electrode surface contains a weak organic acid, HA, the electrode potential will be given by

$$E = E_o + (\mathrm{RT/F})\ln([\mathrm{H^+}]/[\mathrm{HA}]_o) \qquad (24)$$

where $[H^+]$ is the hydrogen-ion concentration in an equilibrium aqueous phase and $[HA]_o$ is the equilibrium concentration of acid in the organic phase. If the aqueous phase also contains metal ions, M^{n+}, which can form an extractable chelate complex MA_n with the reagent HA we have

$$K_{ex} = [\mathrm{MA}_n]\,[\mathrm{H^+}]^n/[\mathrm{M}^{n+}]\,[\mathrm{HA}]_o^n \qquad (25)$$

where the extraction constant, K_{ex} is the equilibrium constant for the heterogeneous reaction

$$\mathrm{M}^{n+} + n(\mathrm{HA})_o \rightleftharpoons (\mathrm{MA}_n)_o + n\mathrm{H^+} \qquad (26)$$

If the value of K_{ex} is sufficiently large initially all the reagent is converted into its metal chelate so that the total amount of reagent $C_{HA} = n[MA_n]_o$ and from Equations 24 and 25

$$E = E_o + (\mathrm{RT}/n\mathrm{F})\,(\ln K_{ex} + \ln n - \ln C_{\mathrm{HA}}) + (\mathrm{RT}/n\mathrm{F})\ln[\mathrm{M}^{n+}] \qquad (27)$$

which under certain circumstances will reduce to

$$E = \text{constant} - (0.0591/n)\,\mathrm{pM}^{n+} \qquad (28)$$

implying that a tenfold change in metal-ion concentration will produce a change of potential of 59.1, 29.5, or 19.7 mV at 25°C according as $n = 1, 2$, or 3. It follows that (1) the larger the extraction constant, K_{ex}, the more positive the potential, and (2) the higher the (fixed) concentration of the reagent C_{HA}, in the organic phase, the more negative the potential. The constancy of C_{HA} must be maintained and losses that would occur in very alkaline solutions or strongly metal-complexing media must be avoided. It is customary to fill the electrode with a solution of the metal chelate, MA_n, in the organic phase rather than one with the ligand HA; this enables the electrode to reestablish the original potential readily, a procedure greatly facilitated if K_{ex} is large.

A closer analysis of the equilibria reveals that the response of the electrode will not be influenced by hydrogen ions provided $[H^+]^n \leqslant n[M^{n+}]K_{ex}\,[HA]^{n-1} / 100$, a condition again favored by a high value of K_{ex}.[226] If applied to dithizone and dithizonates ($HA \equiv H_2Dz$; $MA_n \equiv M(HDz)_n$ it is easily shown that the mercury-sensitive liquid-state electrode will be the least influenced by hydrogen ions, while those of zinc and lead will be considerably influenced as shown in Table 4.

If a liquid-state electrode of the type MA_n is immersed in a solution containing foreign ions H^+ and N^{p+} in addition to M^{n+} we now note that

TABLE 4

The Potential of Liquid-State Metal Dithizonate/CCl_4 Electrodes Showing Increasing Sensitivity to Hydrogen Ions

Electrode sensitive to	Compound in organic phase	pH	E/mV*	log K_{ex}
Hg^{2+}	$Hg(HDz)_2$	3	+475	26.8
Ag^+	$Ag(HDz)$	5	+360	7.2
Cu^{2+}	$Cu(HDz)_2$	5	+250	10.4
Zn^{2+}	$Zn(HDz)_2$	5	+50	1.8
Pb^{2+}	$Pb(HDz)_2$	5	+60	0.4
H^+	H_2Dz	5	−50	—

* Measurements against a standard calomel electrode for ion-electrode immersed in 1×10^{-3} *M* metal nitrate in nitric acid at the pH specified.

$$C_{HA} = n[MA_n]_o + p[MA_p]_o + [HA]_o \qquad (29)$$

and a more complex equation arises for the potential *E*, for account must now be taken of the relative amounts of the three ions and an additional extraction constant K'_{ex} for the interfering reaction

$$N^{p+} + p(HA)_o \rightleftharpoons (NA_p)_o + pH^+ \qquad (30)$$

However the expression for *E* reduces to the simple Nernstian from (28) under certain conditions,[226] and it will be obvious that the selectivity of the M^{n+} ion-sensitive electrode will be greatest when the extraction constant, K_{ex} for the formation of its metal chelate MA_n is greatest and the selectivity will decrease in the order gold(III) > mercury(II) > silver(I) > copper(II) > zinc(II) > lead(II), although this order would be modified if hydrolysis or masking of M^{n+} takes place.

2. *Applications*

Růžička and Tjell describe in considerable detail the construction of liquid-state electrodes incorporating dithizone or metal dithizonates and their response to change in pH and metal ion concentration.[226] In view of its volatility, low viscosity and ease of oxidation to phosgene and other products that attack dithizonates, carbon tetrachloride was rejected as the organic solvent in favor of xylene, benzene, toluene, or mesitylene.

Analytical applications of an Ag^+-selective electrode incorporating Ag(HDz) in xylene were first reported in 1970;[226] in the same year Christian and Stucky described an ion-selective membrane electrode obtained by casting polyvinylchloride, a plasticizer, and dithizone dissolved in cyclohexane. When immersed in $Pb(NO_3)_2$ solution this effectively became a lead dithizonate electrode and was used potentiometrically for Pb^{2+}.[227-228] The cell SCE/10^{-6} *M* $Pb(NO_3)_2$| semipermeable selective membrane| saturated NH_4NO_3|SCE was tested by Lal and Christian in many titrations.[229]

Lal used a dithizone-impregnated perm-selective electrode as an indicator electrode in the potentiometric titration of $AgNO_3$ and Na_2WO_4, and for titrating 10^{-1} to 10^{-3} *M* Ag^+ with sodium oxalate, potassium ferrocyanide, and potassium iodide with average errors of −1.6, −0.8 and −1.7 to +3.7%, respectively.[230,231] With Christian he reported the ascorbimetric titration of silver.[232]

Vanni and Daniele used a solution of mercury(II) dithizonate in benzene as the active phase to give a reversible electrode over the range pH 0.8 to 2.5 with an almost Nernstian response of 30 ±0.5 mV/pHg unit at 25°C for solutions of Hg^{2+} (10^{-1} to 10^{-5} *M*) in 0.5 *M*-KNO_3. This Hg^{2+}-sensitive electrode was used for the potentiometric determination of Al^{3+}, Ca^{2+}, Cu^{2+}, Hg^{2+}, Ni,$^{2+}$ and Zn^{2+} with EDTA, and the titration of EDTA with Hg^{2+}. The relative error was less than 4% in the derivative titration of 2 to 4 × 10^{-3} *M* Ca^{2+} in the presence of Zn^{2+}, and at pH 6 these two ions could be titrated successively in a mixture.[233] Cosofret has tested an $Ag(HDz)/CCl_4$ electrode sensitive for Ag^+ in the range 10^{-1} to 10^{-6} *M*, only Hg^{2+} interfering.[235]

Baiulescu and co-workers have been active in the design of ion-selective electrodes, the most significant advance being an electrode selective to mercury(I).[17] If prepared from a solution of primary $Hg_2(HDz)_2$ it had a Nernstian response of 30 mV/decade over the range 10^{-1} to 10^{-6} *M*, but became unusable after about a week's use with mercury(I) chloride and became insensitive immediately on contact with 0.1 *M* 2,4-dichlorophenoxyacetic acid. On the other hand, an electrode made with palladium dithizonate, $Pd(HDz)_2$, in chloroform had improved selectivity and exceptional stability. No loss of performance was observed after 14 months of daily use and the electrode could be used in acids up to 4 *N*. It could not be poisoned and the internal solution retained its properties even after being boiled for 8 hr.

The behavior of the electrode can be explained by the following equilibrium

$$Hg_2(NO_3)_2 + 2Pd(HDz)_2 \rightleftharpoons Hg_2(HDz)_2 + 2PdDz + 2HNO_3 \qquad (31)$$

since in the presence of mercury (I) ions it is effectively transformed into a Hg(I) dithizonate electrode responsive to Hg_2^{2+}. Similarly, if placed in a solution containing silver ions, Ag(HDz) is formed and the systerm responds to changes in $[Ag^+]$. In the presence of halide ions equilibrium (31) shifts to the left so that, if after use the electrode is washed with 0.1 *M* potassium iodide made slightly acidic with HNO_3 the initial palladium dithizonate is regenerated and in this "inactive" state can be dried and stored.

This versatile electrode was tested in the titration of mercury(II) chloride wherein chloride ions are first set free by KI and after acidification with 0.05 *M* HNO_3 back-titrated with standard 10^{-1} to 10^{-2} *N* $Hg_2(NO_3)_2$. The titration curve shows two jumps—the first corresponding to the titration of excess iodide, the second the simultaneous titration of Cl^- and Hg_4^{2-}. Mercury (I) chloride, mercury (II) oxide are among mercury compounds that can be titrated directly, those of organomercury compounds becoming titratable after wet-ashing. Examples are also given of the titration of Hg_2^+, Hg^{2+} and Ag^+ alone or in mixtures and the analysis of organic substance such as phthalic acid, pyrethrins and formic acid, aldehydes, hydroxylamine, hydrazine and its derivatives, and the potentiometric determination of I^-, Br^-, and Cl^- alone and in a mixture.[17]

E. Additional Applications

1. Qualitative Tests

In the early days dithizone was much used as a qualitative reagent, and still serves as a selective reagent for detecting segregation of, e.g., lead in steels or brasses, and for sundry alloying agents or impurities in magnesium or aluminum base alloys,[3,12] and more recently for detecting zinc octanoate in mothproofing wool.[236] It continues to be used as a stain for zinc in histochemical studies, although, because of its ability to complex zinc, it has gained much importance as a means of inducing experimental diabetes.

2. Ligand and Metal Exchange

The replacement of one ligand by another is an interesting process, which Starý et al. have considered in much detail;[159] yet apart from a method for the determination of arsenic the principle does not seem to have been adequately exploited for spectrophotometric determinations.[72] However, Grey and Cave have shown that Ag, Cu(II), Cd, In, and Pb can be determined by first extracting with H_2Dz/CCl_4 and then displacing the dithizone by titrating with a standard solution of sodium diethyldithiocarbamate in ethanol.[237]

Metal ion displacement is another technique that has largely been neglected. If, e.g., a solution of Ag(HDz) in CCl_4, labeled with ^{110}Ag, is equilibriated with an aqueous phase containing an unknown amount of Ag^+ isotope, exchange takes place rapidly and the activity in the aqueous phase is a measure of the amount of inactive silver originally present.[3] A comparable procedure is a method for the determination of traces of mercury in which Hg^{2+} displaces $^{65}Zn^{2+}$ from a labeled solution of $Zn(HDz)_2$.[135] With inactive Ag(HDz) soaked on filter paper, metal ion replacement by Hg^{2+} to give $Hg(HDz)_2$ produces a colored zone whose area is a measure of the mercury(II) ion that has reacted.[136] The same principle is used, of course, in displacement chromatography, e.g., for separating zinc from cadmium on a column loaded with $Pb(HDz)_2$, or mercury from copper on a column loaded with Ag(HDz).[66]

An allied principle has been applied to the determination of traces of iodide (0 to 50 μg), which strips a certain amount of metal (as HgI_4^{2-}) from $Hg(HDz)_2$ so producing a decrease in absorbance that can be measured spectrophotometrically.[238] On the other hand, traces of bromide can be extracted into chloroform as the complex, $HgBr_2$ (isoquinoline)$_2$, and on subsequent ligand substitution with dithizone the initial Br^- is measured spectrophotometrically in terms of the $Hg(HDz)_2$ formed. As might be expected Cl^-, I^-, Cr,$^-$ and SCN^- interfere.[239]

3. Titrimetry

As an indicator in titrimetry dithizone continues to be used in various ways. For example, Ohmact uses it to determine the endpoint of an argentometric titration of halides obtained after combusting organic substances by the Schöniger flask method.[240] Fano et al. use it as an endpoint indicator in the form of its cadmium complex when titrating alkaline earths with EDTA at pH 10.5; excess of titrant causes the color to change from red to green.[241] When determining Ca in the presence of small excess of Mg, Sr, or Ba the metal is complexed with excess EDTA at pH 9.5 and the excess back-titrated with Ca using a Cd-dithizone indicator.[241] Similarly aluminum in ferrochrome slag can be complexed with excess EDTA and this excess determined by back-titration with standard zinc when the color change of dithizone from green to red marks the endpoint.[242]

Many papers have been published describing the use of analogues of dithizone as extraction indicators;[243] they seldom make any claims for using them in preference to dithizone.

The original technique of extractive titration seems to have fallen largely into disuse, probably because it is difficult to carry out experimentally and quite time-consuming.[3,12] A continuous two-phase extraction in which the absorption spectrum of the organic phase is continuously monitored is a more promising alternative,[3,12] and Galík has compared the merits of dithizone as a titrant with those 1-(2-pyridylazo)-2-naphthol.[244] PAN is actually more selective than dithizone towards cadmium and zinc (and not affected by palladium or mercury), but it is of course not so sensitive. Mukhamedzhanova et al. state that titration of Ag, Hg(I) and (II), Cd and Pd with H_2Dz/CCl_4 or C_6H_6 is as sensitive using an amperometric endpoint as by spectrophotometry.[173]

4. Kinetic Effects

The different rates at which certain metals are extracted by dithizone has been discussed previously and the differences can be exploited as a means of achieving greater selectivity.[3,245] The effect of pyridine in modifying the rate of extraction of e.g., manganese,[115] has been extended to an examination of the effects of other auxiliary complexing reagents.[198] Vinokurova and Kletenik have recently made a fresh study of the rate of extraction of Co, Cu, Ni, and Zn by $H_2Dz/CHCl_3$ and in addition to interpreting the new data they make a number of proposals for increasing the selectivity of liquid-liquid extractions of metal dithizonates making use of kinetic factors.[246] Another recent observation that merits closer attention is the effect of ultrasound (15 Hz) on the extraction of Bi, Co, Cu, and Zn as dithizonates into CCl_4 at 25°C.[247] In most cases the rate of extraction is increased by 50% and it is stated that the distribution coefficient is also changed by as much as 33%.

5. Concluding Remarks

Although 50 years have elapsed since it was first introduced, dithizone continues to play a valuable role in analytical chemistry. To be sure the initial emphasis on spectrophotometric finishes has lost some impact in view of the widespread use of atomic absorption spectrophotometry and other physical procedures. At the same time, the special characteristics of the reagent and its metal complexes lend themselves to those procedures for preconcentrating and separating traces of metals of paramount importance in contemporary environmental analysis; its versatility is reflected in the new applications which appear from time to time. No longer a young reagent, it still continues to enjoy a fruitful middle age.

REFERENCES

1. Fischer, H., *Wiss. Veroff. Siemens-Werken*, 4, 158 (1925).
2. Iwantscheff, G., *Fresenius' Z. Anal. Chem.*, 280 (2), 97 (1976).
3. Irving, H. M. N. H., *Dithizone*, Analytical Sciences Monograph No. 5., Chemical Society, London, 1977.
4. Gran, G., *Sven. Papperstidn.*, 53, 234 (1950).
5. Webb, J. L. A., Bhatia, I. S., Corwin, A. H., and Sharp, A. G., *J. Am. Chem. Soc.*, 72, 91 (1950).
6. Aldridge, W. N. and Cremer, J. E., *Analyst (London)*, 82, 37 (1957).
7. Irving, H. and Cox, J. J., *J. Chem. Soc.*, p. 1470 (1961).
8. Růžička, J. and Starý, J., *Talanta*, 8, 228 (1961); 9, 617 (1962).
9. Starý, J. and Růžička, J., *Talanta*, 8, 296 (1961).
10. Růžička, J. and Starý, J., *Talanta*, 8, 535 (1961).
11. Růžička, J. and Starý, J., *Talanta*, 9, 617 (1962).
12. Iwantscheff, G., *Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse*, 2nd ed., Verlag Chemie, Weinheim, 1972.
13. Janardhan, P. B. and Rajeswari, S., *Curr. Sci.*, 45(10), 373 (1976).
14. Fano, V. and Zanotti, L., *Anal. Chim. Acta*, 72, 419 (1974).
15. Marczenko, Z. and Podsiadlo, E., *Mikrochim. Acta*, 2(3—4), 317 (1976).
16. Lee, Y. K., Whang, K. J., and Ueno, K., *Talanta*, 22, 535 (1975).
17. Baiulascu, G. E. and Ciocan, N., *Talanta*, 24, 37 (1977).
18. De, A. K., Khopkar, S. M., and Chalmers, R. A., *Solvent Extraction of Metals*, Van Nostrand & Reinhold, London, 1970.
19. Morrison, G. H., and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, (1966).

20. Reynolds, R. J., *Dithizone: Reagent for Lead,* Monograph No. 30, 1956; *Dithizone: Reagent for Mercury, Zinc, Cadmium, and Bismuth,* Monograph No. 32, Hopkins & Williams, London, (1957).
21. Sandell, E. B., *Colorimetric Determination of Traces of Metals,* 3rd ed., Interscience, New York, 1959.
22. Starý, J., *Solvent Extraction of Metal Chelates,* Pergamon Press, Oxford, (1964).
23. Zolotoff, Yu. A., *Extraction of Chelate Compounds,* Humphrey Scientific Publications, Ann Arbor, (1970).
24. Kiwan, A. M. and Kassim, A. Y., *Anal. Chim. Acta,* 88(1), 177 (1977).
25. Fischer, E. and Besthorn, E., *Justus Liebigs Ann. Chem.,* 212, 316 (1882).
26. Bamberger, E., Padova, R., and Ormerod, E., *Justus Liebigs Ann. Chem.,* 446, 260 (1926).
27. Laing, M., *J. Chem. Soc. Dalton Trans.,* 2, 1248 (1977).
28. Carlin, C. H., Ph.D. dissertation, John Hopkins University, Baltimore, 1966.
29. Irving, H. M. N. H. et al., unpublished results.
30. Coleman, R. A., Foster, W. H., Kazan, J., and Mason, M., *J. Org. Chem.,* 35(6), 2039 (1970).
31. Spěváček, V. and Spěváčková, V., *J. Inorg. Nucl. Chem.,* 38, 1299 (1976).
32. Akaiwa, H. and Kawamoto, H., *J. Inorg. Nucl. Chem.,* 29, 541 (1967).
33. McDonald, W. S., Irving, H., Raper, G., and Rupainwar, D.C., *J. Chem. Soc.,* D(8), 392 (1969).
34. Geiger, R. W. and Sandell, E. B., *Anal. Chim. Acta,* 8, 197 (1953).
35. Meriwether, L. S., Breitner, E. C., and Colthup, N. B., *J. Am. Chem. Soc.,* 87, 4448 (1965).
36. Irving, H. M. N. H. and Kiwan, A. M., *Anal. Chim. Acta,* 45, 271 (1969).
37. Irving, H. M. N. H., Naqvi, N. F., and Tilley, C. G., *Anal. Chim. Acta,* 100, 597 (1978).
38. Starý, J. and Freiser, H., *Equilibrium Constants of Liquid-Liquid Distribution Reactions,* Part 4, IUPAC Additional Publication, Pure and Applied Chemistry, Butterworths, London, 1976.
39. Uesugi, K. and Freiser, H., *Analytical Chemistry: Essays in Memory of Anders Ringbom,* Wanninen, E., Ed., Pergamon Press, Oxford, (1977).
40. Irving, H. M. N. H., Kiwan, A. M., Rupainwar, D. C., and Sahota, S. S., *Anal. Chim. Acta,* 56, 205 (1971).
41. King, H. G. C. and Pruden, G., *Analyst (London),* 96, 146 (1971).
42. Meriwether, L. S., Breitner, E. C., and Sloan, C. L., *J. Am. Chem. Soc.,* 87, 4441 (1965).
43. Kisfaludi, G. and Lenhof, M., *Anal. Chim. Acta,* 54, 83 (1971).
44. Matkovich, C. E. and Christian, G. D., *Anal. Chem.,* 46, 102 (1974).
45. Marczenko, Z. and Mojski, M., *Chim. Anal. (Paris),* 54, 29 (1972).
46. Henderson, S. R. and Snyder, L. T., *Anal. Chem.,* 33, 1172 (1961).
47. Kasterka, B. and Kwiatkowska-Sienkiewicz, K., *Chem. Anal. (Warsaw),* 18, 1153 (1973).
48. Ashizawa, T., Sugizaki, S., Asahi, H., Sakai, H., and Shibata, K., *Bunseki Kagaku,* 19(10), 1333 (1970); *Chem. Abstr.,* 74, 38037h, (1971).
49. Jedrzejewski, S. and Jedrzejewska, H., *Chem. Anal. (Warsaw),* 15(4), 729 (1970).
50. Concialini, V., Lanza, P., and Lippolis, M. T., *Anal. Chim. Acta,* 52, 529 (1970).
51. Muchova, A. and Jokl, V., *Chem. Zvesti,* 22(1), 62 (1968); *Chem. Abstr.,* 68, 119017e, (1968).
52. Muchova, A. and Jokl, V., *Acta Fac. Pharm. Univ. Comenianae,* 17, 99 (1969).
53. Massa, V., *Farmaco, Ed. Prat.,* 25(5), 332 (1970). *Chem. Abstr.,* 73, 38607g, 1970.
54. Takitani, S., Suzuki, M., Namai, T., and Nagato, F., *J. Hyg. Chem. (Japan), 16(2),* 83, (1970); *Chem. Abstr.,* 73, 72748c, (1970).
55. Yamane, Y., Miyazaki, M., Iwase, H., and Takeuchi, T., *J. Hyg. Chem. (Japan),* 16, 254, (1970); *Chem. Abstr.,* 75, 52645g, (1971).
56. Sebesta, F., *J. Radioanal. Chem.,* 7(1), 41 (1971).
57. Gregorowicz, Z., Kulicka, J., and Suwinska, T., *Chem. Anal. (Warsaw),* 16(1), 169 (1971); *Chem. Abstr.,* 74, 150765v, (1971).
58. Lautenschläger, W., Pahlk, S., and Tölg, G., *Fresenius' Z. Anal. Chem.,* 260, 203 (1972).
59. Portillo, R. Moya-Angeler and Palomeque, B. E., *Cienc. Ind. Farm.,* 8(2), 45 (1976).
60. Portillo, R. Moya-Angeler and Palomeque, B. E., Cienc. Ind. Farm., 8(9), 258 (1976); *Chem. Abstr.,* 86, 100412c, (1977).
61. Tattor, J. O. G. and Wagstaffe, P. J., *J. Chromatogr.,* 44(2), 284 (1969).
62. Braun, D. and Heines, H.-Th., *Fresenius' Z. Anal. Chem.,* 239, 6 (1968).
63. Takeshita, R., Akagi, H., Fujita, M., and Sakagami, Y., *J. Chromotogr.,* 51(2), 283, (1970).
64. Busev, A. I., Kharlamov, I. P., and Smirnova, O. V., *Anal. Lett.,* 3(4), 177 (1970).
65. Kharlamov, I. P., Smirnova, O. V., and Busev, A. I., *Tr. Tsentr. Nauchno — Issled. Inst. Tekhnol. Mashinostr.,* 110, 16 (1972); *Chem. Abstr.,* 80, 77933r, (1974).
66. Lorber, K., Mueller, K., and Spitzy, H., *Mikrochim. Acta,* 2(6), 603 (1975).
67. Spěváčková, V. and Křivánek, M., Proc. 3rd Anal. Chem. Conf., Vol. 1, Buzas, I., Ed., Akad. Kiado, Budapest, Hungary, 1970, 121; *Chem. Abstr.,* 74, 49263e, 1971.

68. Galik, A., *Anal. Chim. Acta,* 67, 357 (1973).
69. Bauman, A. J. and Richards, J. H., *Sep. Sci.,* 6(5), 715 (1971).
70. Shoji, H., Mabuchi, H., and Saito, N., *Bull. Chem. Soc. Jpn.,* 47, 2502 (1974); *Chem. Abstr.,* 82, 8221m, (1975).
71. Kamada, T. and Yamamoto, Y., *Talanta,* 24(5), 330 (1977).
72. Sebesta, F. and Stary, J., *Collect. Czech. Chem. Commun.,* 33, 3895 (1968).
73. Levitman, Kh. Ya., Korol, L. S., and Specktor, A. L., *Dokl. Akad. Nauk SSSR,* 21(4), 332 (1977); *Chem. Abstr.,* 87, 33245h, (1977).
74. Analytical Methods Committee, *Analyst (London),* 94, 1153 (1969).
75. Yamada, E. and Namiki, H., *Kogyo Yosui,* 190, 21 (1974); *Chem. Abstr.,* 82, 7419v, (1975).
76. Ashizawa, T. and Hosoya, K., *Bunseki Kagoku,* 20, 1416 (1971); *Chem. Abstr.,* 76, 54041b, (1972).
77. Tumanov, A. A. and Shakhverdi, N., *Zavod. Lab.,* 36(8), 918 (1970); *Chem. Abstr.,* 74, 9272a, (1971).
78. Roberts, A. H. C., Turner, M. A., and Sykes, J. K., *Analyst (London),* 101, 574 (1976).
79. Kasparec, I., Zeman, A., and Prasilova, J., *J. Radioanal. Chem.,* 2, 281 (1969).
80. Lorber, K. and Mueller, K., *Mikrochim. Acta,* 1(2,5), 325, (1977).
81. Akaiwa, H., Kawamoto, H., and Hara, M., *J. Chem. Soc. Jpn. Pure Chem. Sect.,* 90(4), 186, (1969); *Chem. Abstr.,* 70, 111304, (1969).
82. Kemula, W., Janowski, A., and Ganko, T., *Rocz. Chem.,* 46, 1235 (1972).
83. Murata, M. and Kitao, A., *Bunseki Kagaku,* 19(9), 1287 (1970); *Chem. Abstr.,* 74, 27755q, (1971).
84. Salvato, B., *Bull. Soc. Ital. Biol. Sper.,* 48, 1314, 1972.
85. Florence, T. M. and Batley, G. E., *Talanta,* 24, 151 (1977).
86. Halldor, A., *Anal. Chim. Acta,* 88(1), 89 (1977).
87. Gevorgyan, A. M., Talipov, Sh. T., and Khadeev, V. A., *Chem. Abstr.,* 86, 182552n, (1977).
88. Hiraide, M. and Mizuike, A., *Talanta,* 22, 539 (1975).
89. Jamro, G. H. and Frei, R. W., *Mikrochim. Acta,* 3, 429 (1970).
90. Roth, F. and Gilbert, E., *Mitt. Rebe Wein Ostbau Freuchtwert (Klosterberg),* 19(6), 430 (1969).
91. Iwantscheff, G. and Jörrens, Ch., *Fresenius' Z. Anal. Chem.,* 264, 131 (1973).
92. Cox, J. J. and Servant, D. M., *Anal. Chim. Acta,* 66, 123 (1973).
93. Beardsley, D. A., Briscoe, G. B., Růžička, J., and Williams, M., *Talanta,* 13, 328, (1966).
94. Petrukhin, O. M., Demina, L. A.and Zolotov, Yu. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk,* 4, 72 (1970); *Chem. Abstr,* 74, 80381r, (1971).
95. Zolotov, Yu. A., Demina, L. A. and Petrukhin, O. M., *Zh. Anal. Khim.,* 25(12), 2315 (1970); *Chem. Abstr.,* 74, 80389z, (1971).
96. Cox, J. J. and Servant, D. M., *Anal. Chim. Acta,* 74, 200 (1975).
97. Marczenko, Z. and Mojski, M., *Chim. Anal. (Paris),* 53(8), 529 (1971).
98. Zolotoff, Yu. A., Kiselva, O. A., Shakova, N. V., and Lebedev, V. I., *Anal. Chim. Acta,* 79, 237 (1975).
99. Groffman, D. M. and Wood, R., *Analyst (London),* 96, 140 (1971).
100. Heller, A. and Kettner, H., *Schriftenr. Ver. Wasser-, Boden-, Lufthyg., Berlin-Dahlem,* 29, 3 (1969); 29, 51 (1969).
101. Oelschläger, W. and Schwarz, E., *Fresenius' Z. Anal. Chem.,* 258, 203 (1972).
102. Oelschläger, W. and Frenkel, E., *Landwirtsch. Forsch,,* 26, 281 (1973).
103. Pierce, J. O. and Meyer, J. H., *Atmos. Environ.,* 5(9), 811 (1971).
104. Donovan, P. P. and Feeley, D. T., *Analyst (London),* 94, 879 (1969).
105. Matsumoto, I., Okamoto, M., and Saruwatari, K., *J. Hyg. Chem. (Japan),* 17, 84 (1971); *Chem. Abstr,* 75, 52676, 1971.
106. Bratzel, M. P. and Chakrabarti, C. L., *Anal. Chim. Acta,* 61, 25 (1972).
107. Karbainov, Yu. A. and Stromberg, A. G., *Izv. Tomsk. Politekh. Inst.,* 174, 24 (1971).
108. Fano, V., Licci, F., and Zanotti, L., *Microchem. J.,* 19, 163 (1974).
109. Vydra, F. and Nghi, T. V., *Electroanal. Chem. Interfacial Electrochem.,* 78(1), 167 (1977).
110. Shendrikar, A. D. and West, P. W., *Anal. Chim. Acta,* 61, 43 (1972).
111. Postlethwaite, R. T., Kidman, L., Bagshawe, B., Bills, K. M., Harrison, T. S., and Watt Smith, J. A., *J. Iron Steel Inst., London,* 208(5), 500 (1970).
112. Benini, F. and Covella, M., *Quad. Sclavo Diagn. Clin. Lab.,* 6(2), 388 (1970); *Chem. Abstr.,* 74, 108008a, 1971.
113. Fauran, F., Gras, G., and Mane, B., *Analusis,* 4(1), 34, (1976).
114. Hancock, S. and Slater, A., *Analyst (London),* 100, 422 (1975).
115. Akaiwa, H. and Kawamoto, H., *Anal. Chim. Acta,* 40, 407 (1968).
116. Marczenko, Z. and Mojski, M., *Anal. Chim. Acta,* 54(3), 469 (1971).
117. Krylova, A. N., *Sud-Med. Ekspert.,* 17, 38 (1974); *Chem. Abstr.,* 82, 52268f, 1975.

118. Naito, S., Kaneko, M., Setsuda, S., Matsuzaki, J., Ogura, M., Fukui, S., and Kanno, S., *Eisei Kagaku,* 15(5), 312 (1969); *Chem. Abstr.,* 72, 97225z, 1970.
119. Palalau, L., *Rev. Chim. (Bucharest),* 20, 107 (1969).
120. Pakter, M. K., *Gig. Sanit.,* 34, 70 (1969); *Chem. Abstr.,* 71, 53265, 1969.
121. Ohta, N. and Terai, M., *Bull. Chem. Soc. Jpn.,* 44, 1153 (1971).
122. Macovschi, M. E. and Nitu, V., *Chim. Anal. (Bucharest),* 14, 232 (1971); *Chem. Abstr.,* 76, 148491, (1972).
123. Litman, R., Williams, E. T., and Finston, H. L., *Anal. Chem.,* 49(7), 983 (1977).
124. Briscoe, G. B. and Cooksey, B. G., *J. Chem. Soc.,* A(2), 205 (1969).
125. Shater, K. S., Erimina, A. F., Semeryakova, A. I., Smirnov, V. V., and Efremov, A. V., *Zavod. Lab.,* 36(12), 1470 (1970); *Chem. Abstr.,* 74, 57127d, (1971).
126. Osajima, Y., Tokubo, M., Nakasima, M., Matsumoto, K., Hashinaga, F., and Furutani, S,. *Kyushu Daigaku Nogakubu Gakugei Zasshi,* 26, 525 (1972); *Chem. Abstr.,* 76, 158134, (1972).
127. Chau, Yiu-Kee and Saitoh, H., *Effluent Water Treat. J.,* 11(3), 135 (1971).
128. Massa, V., *Trans. Soc. Pharm. Montpellier,* 28(3), 203 (1968).
129. Kosta, L. and Byrne, A. R., *Talanta,* 16, 1297 (1969).
130. Byrne, A. R., Dermelj, M., and Kostas, L., *J. Radioanal. Chem.,* 6, 325 (1970).
131. Růžička, J. and Lamm, C. G., *Talanta,* 16, 157 (1969).
132. Tahara, I., *Jpn. Kokai,* 71, 769, (1973); *Chem. Abstr,* 80, 38916t, (1974).
133. Yano, T., Ide, S., Tobeta, Y., Kobagashi, H., and Ueno, K., *Talanta,* 23(6), 457 (1976).
134. Ide, S., Yano, T., and Ueno, K., *Bunseki Kagaku,* 25(12), 820 (1976); *Chem. Abstr.,* 86, 176934x, (1977).
135. Curry, J. and Merron, M. P., *J. Radioanal. Chem.,* 34(2), 319 (1976).
136. Kielczewski, W., Tornkowiak, J., and Uchman, W., *Chem. Anal. (Warsaw),* 16, 529 (1971); *Chem. Abstr.,* 76, 31134v, (1972).
137. Irving, H. M. N. H. and Kiwan, A. M., *Anal. Chim. Acta,* 45(2), 243 (1969); 45(2), 255 (1969); 45(3), 447 (1969).
138. Kiwan, A. M. and Fouda, M. F. R., *Anal. Chim. Acta,* 40, 517 (1968).
139. Gorgia, A. and Monnier, D., *Anal. Chim. Acta,* 55(1), 247 (1971).
140. Zamyslova, S. D. and Ashmarina, N. P., Vopr. G.'g. Vody Sanit. Okhr. Vodoemov, 138, (1968); *Chem. Abstr.,* 71, 84350r, (1969).
141. Suenaga, S. and Shiraishi, Y., *Eisei Kagaku,* 16(2), 71 (1970); *Chem. Abstr.,* 73, 91027k, (1970).
142. Murakami, T. and Yoshinga, T., *Jpn. Anal.,* 20, 878 (1971); *Chem. Abstr.,* 75, 91107, (1971).
143. Kiwan, A. M. and Fouda, M. F. R., *J. Organometl. Chem.,* 23(1), 9 (1970).
144. Kambara, T., and Hara, M., *Bull. Chem. Soc. Jpn.,* 44, 1040 (1971); *Chem. Abstr.,* 75, 29594, (1971).
145. Tomcsanyi, L., *Anal. Chim. Acta,* 89(2), 409 (1977).
146. Al'bota, L. A, Serdyuk, L. S., and Zaverach, M. M., *Dopov. Akad. Nauk Ukr. RSR, Ser. B.,* 36, 437 (1974); *Chem. Abstr.,* 81, 57699m, 1974.
147. Math, K. S. and Freiser, H., *Anal. Chem.,* 41(12), 1682 (1969).
148. Math, K. S., Bhatki, K. S., and Freiser, H., *Talanta,* 16, 412 (1969).
149. Briscoe, G. B. and Humphries, S., *Talanta,* 18(1), 39 (1971).
150. Colonat, J. F., Report 1975 LYCEN-7569. *Chem. Abstr.,* 85, 113195n, (1976).
151. Eckelmans, V., Graauwmans, E., and de Jaegere, S., *Talanta,* 21, 715 (1974).
152. Minczewski, J., Krasiejko, M., and Marczenko, Z., *Chem. Anal. (Warsaw),* 15(1), 43 (1970).
153. Shcherbov, D. P., Gladysheva, G. P., Ivankova, A. I., and Vredenskay, I.D., Zhur. Khim., 1974 Abstr. No. 13 G 150; *Chem. Abstr.,* 82, 148998v, (1975).
154. Rakovskii, E. E., Krylova, T. D., Starozhitskaya, M. I., and Frolova, A. Yu., *Zh. Anal. Khim.,* 28, 1554 (1973); *Chem. Abstr.,* 80, 22324n, (1974).
155. Keihei, V., *Jpn. Kokai,* 74 10,089; *Chem. Abstr.,* 80, P-40894w,(1974).
156. Mabuchi, H. and Nakahara, H., *Bull. Soc. Chim. Jpn.,* 36, 151 (1963).
157. Shcherbov, D. P., Ivankova, A. I., and Gladysheva, G. P., *Zavod. Lab.,* 33, 683 (1967).
158. Kasterka, B. and Dobrowolski, J., *Chem. Anal. (Warsaw),* 15(2), 303, (1970); *Chem. Abstr.* 73, 62373q, (1970).
159. Starý, J. and Růžička, J., *Talanta,* 15, 689 (1968).
160. Ramakrishna, R. S. and Irving, H., *Anal. Chim. Acta,* 49(1), 9 (1970); cf. *J. Chem. Soc.,* D23, 1356, 1969.
161. Starý, J. and Marek, J., *Chem. Commun.,* 519, (1970).
162. Starý, J., Marek, J., Kratzer, K., and Sebesta, F., *Anal. Chim. Acta,.* 57, 393 (1971).
163. Boenig, G. and Heigener, H., *Landwirtsch. Forsch.,* 23(3), 258 (1970).

164. Jordanov, N. and Daskalova, K., *Dokl. Bolg. Akad. Nauk*, 23(8), 969 (1970); *Chem. Abstr.*, 74, 60610m, (1971).
165. Ivankova, A. I., Gladysheva, G. P., and Shcherbov, D. P., *Issled. Obl. Khim. Fiz. Metodov Anal. Miner. Syr.*, 4, 29, 1975; *Chem. Abstr*, 87, 77839i, (1977).
166. Shcherbov, D. P. Ivankova, A. I., and Gladysheva, G. P., *Zh. Anal. Khim.*, 32(1), 105 (1977); *Chem. Abstr.*, 87, 77822y, (1977).
167. Wichrowska, B., *Rocz. Panstw. Zakl. Hig.*, 22, 561 (1971); *Chem. Abstr.*, 76, 37254f, (1972).
168. Fukai, R., Huynh-Ngoc-Lang, *Nippon Kaiyo Gakkai-Shi*, 27, 91, (1971); *Chem. Abstr.*, 76, 37236b, (1972).
169. Macovschi, M. E., *Zh. Anal., Khim.*, 25(6), 1226 (1970); *Chem. Abstr.*, 73, 94351x, (1970).
170. Kudo, K. and Hishinuma, N., *J. Radioanal. Chem.*, 5, 331 (1970).
171. Lillie, E. G., *Anal. Chim. Acta*, 75, 21 (1975).
172. Elek, A., Bogancs, J., and Szabo, E., *J. Radioanal. Chem.*, 4(2), 281 (1970).
173. Mukhamedzhanova, D., Talipov, Sh. T., and Khadeev, V. A., *Uzb. Khim. Zh.*, 14(4), 12 (1970); *Chem. Abstr.*, 74, 119706c, (1971).
174. Schnedfe, M. M., *Anal. Chim. Acta*, 79, 101 (1975).
175. Malik, W. V. and Sharma, T. C., *Fresenius' Z. Anal. Chem.*, 258(2), 124 (1972).
176. Analytical Methods Committee of S. A. C., *Analyst (London)*, 93, 414, (1968).
177. Kahara, T. and Takei, S., *J. Inorg. Nucl. Chem.*, 33, 4129 (1971).
178. Mikami, T. and Takei, S., *J. Inorg. Nucl. Chem.*, 33, 4283 (1971).
179. Herold, B. and Droege, K. H., *Fresenius' Z. Anal. Chem.*, 245, 295 (1969).
180. Vrestal, J. and Havir, J., *Chem. Prum.*, 23, 135 (1973); *Chem. Abstr.*, 79, 26934p, (1973).
181. Freitag, K. D. and Bock, R., *Fresenius' Z. Anal. Chem.*, 270, 337 (1974).
182. Zaidi, S. A. A. and Siddiqi, K. S., *Indian J. Chem.*, 11, 1179 (1973).
183. Smoczkiewiczowa, A. and Kokocinska, H., *Pr. Zakresu Towarozn. Chem.*, *Wyzsza Szk. Ekon. Poznaniu, Zesz. Nauk. Ser. 1*, 53, 101 (1974); *Chem. Abstr.*, 82, 32105x, (1975).
184. Tikhomirova, E. I., *Litogeokhimicheskii Metody Poiskakh Skrytogo Orudeneniya*, 100, (1972); *Chem Abstr.*, 81, 20482j, (1974).
185. Vas'kova, A. G., Avilov, V. B., and Mikhalova, N. A., *Vopr. Geol. Geokhim. Metallogen. Sev. Zapod. Sekt. Tikhovkean Poyasa Mater. Nauch. Sess.*, 252, (1969); *Chem. Abstr.*, 75, 94293w, (1971).
186. Zawadska, T. and Sokolwska, R., *Rocz. Panstw. Zakl. Hig.*, 22, 161 (1971); *Chem. Abstr.*, 75, 59633, (1971).
187. Song, M. K., Adham, N. F., and Rinderknecht, H., *Am. J. Clin. Pathol.*, 65(2), 229, (1976).
188. Sikorowska, C. and Wichrowska, B., *Rocz. Panstw. Zakl. Hig.*, 22, 17 (1971); *Chem. Abstr.*, 75, 9740, (1971).
189. El Kadi, M. A., Sabet, S. A., Abdel Salam, M. A., El Sherif, S, and Hamdi, H., *Egypt. J. Soil Res.*, 12, 207 (1972); 12, 123 (1972).
190. Fukai, R., Huynh-Ngoc, L., and Murray, C. N., *J. Oceanog. Sec. Jpn.*, 29, 44 (1973); also see *Estuar. Coast. Mar. Sci.*, 3, 177 (1973).
191. Fukai, R. and Huynh-Ngoc, L., *J. Oceanog. Soc. Jpn.*, 31, 179 (1975).
192. Rastogi, S. K. and Raj. M. M., *Mysore J. Agric. Sci.*, 9(4), 609 (1975); *Chem. Abstr.*, 84, 88499n, (1976).
193. Elsokkary, I. H., *Alexandria J. Agric. Res.*, 23(2), 367 (1975); *Chem. Abstr.*, 85, 19675a (1976).
194. Vrignaud, C., Ducassou, D., Vrignaud, N., and Blanquet, M. P., *Bull. Soc. Pharm. Bordeaux*, 108(4), 169 (1969); *Chem. Abstr.*, 73, 10435s, (1970).
195. Petrov, Ju. M., *Zh. Anal. Khim.*, 29, 686 (1974).
196. Akaiwa, H., Kawamoto, H., and Ogura, K., *Talanta*, 24, 394 (1977).
197. Perrin, D. D., *Talanta*, 24, 339 (1977).
198. Subbaraman, P. R., Cordes, M., and Freiser, H., *Anal. Chem.*, 41(13), 1878 (1969).
199. Yamashita, K., *Rev. Polarogr.*, 15(3), 65 (1968); *Chem. Abstr.*, 70, 16614j, 1969.
200. Sharma, T., Agarwal, R. S., and Agarwal, K. S., *J. Sci. Res. (Hardwar, India)*, 2, 74 (1970).
201. Tomcsanyi, L., *Anal. Chim. Acta.*, 70, 411 (1974).
202. Tomcsanyi, L., *Anal. Chim. Acta*, 88(2), 371 (1977).
203. Klug, O. N., Szucs, A., and Lovasi, J., *Banyasz. Kohasz. Lapok, Kohasz.*, 103(2), 90 (1970); *Chem. Abstr.*, 73, 51943z, (1970).
204. Stromberg, A. G., Karbainov, Yu. A., and Gridaev, V. F., *Izv. Tomsk. Politekh. Inst.*, 164, 231 (1967); *Chem. Abstr.*, 74, 115705, (1971).
205. Gruetzner, G. and Lehmann, R., *Chem. Anal. (Warsaw)*, 19, 287 (1974); *Chem. Abstr.*, 81, 77236b, (1974).

206. Lel'chuk, Y. L., Sokolovich, V. B., and Detkova, G. A., *Tr. Nauch. Konf. Tomsk. Otdel. Vses. Khim. Obshchest 1st*, 167, (1969); *Chem. Abstr.*, 74, 115705d, (1971).
207. Tokuda, S., Ito, Y., Asada, S., and Ito, Y., *Jpn. Kokai*, 74, 44991; *Chem. Abstr.*, 81, 126575g, (1974).
208. Bauman, A. J., Weliky, N., and Weetall, H. H., U.S. Patent 3,484,390 December 1969; *Chem. Abstr.*, 72 P 44604r, (1970).
209. Braun, T. and Farag, A. B., *Anal. Chim. Acta*, 69, 85 (1974); *Anal. Chim. Acta*, 71, 133 (1974).
210. Braun, T. and Farag, A. B., *Anal. Chim. Acta*, 73, 307 (1974).
211. Chow, A. and Buksaj, D., *Can. J. Chem.*, 53, 1373 (1975).
212. Sekizuka, Y., Kojima, T., Yano, T., and Ueno K., *Talanta*, 20, 979 (1973).
213. Ueno, K., Yano, T., and Kojima, T., *Anal. Lett.*, 5(7), 439 (1972).
214. Aggett, J. and West, T. S., *Anal. Chim. Acta*, 57, 15 (1971).
215. Rattonetti, A., *Anal. Chem.*, 46, 739 (1974).
216. Podberezskaya, N. K. and Sushkova, V. A., *Issled. Tsvet. Fluorestsent. Reakts. Opred. Blagorod. Metal*, 118, (1969); *Chem. Abstr.*, 74, 60580b, (1971).
217. Ermenko, V. Ya, and Mel'nikov, E. A., *Gidrokhim. Mater.*, 55, 103 (1971); *Chem. Abstr.*, 75, 121240k, (1971).
218. Sachdev, S. L. and West P. W., *Anal. Chim. Acta*, 44, 301 (1969).
219. Lieberman, K. W. and Kramer, H. H., *Anal. Chem.*, 42, 266 (1970).
220. Mizuno, T., Harada, A., Kudo, Y., and Hasegawa, N., *Jpn. Anal.*, 19, 251 (1970).
221. Kudo, K. and Hishinuma, N., *J. Radioanal. Chem.*, 3, 369 (1969).
222. Obrusnik, I., *Talanta*, 16, 563 (1969).
223. Spěváčková, V. and Křivánek, M., *J. Radioanal. Chem.*, 21, 488 (1974).
224. Elek, A. and Szabo, E., *Solvent Extr., Proc. Int. Solvent Extr. Group*, 2, 1101, 1971. Gregory, J. G., Evans, B., and Weston, P. C., Eds., Society for Chemical Industry, London; *Chem. Abstr.*, 84, 11837p.
225. Moody, G. J. and Thomas, J. D. R., *Sel. Annu. Rev. Anal. Sci.*, 3, 59 (1973).
226. Růžička, J. and Tjell, J. Chr., *Anal. Chim. Acta*, 51(1), 1 (1970).
227. Christian, G. D. and Stucky, G. L., *Am. Lab.*, p. 18 (October 1970).
228. Stucky, G. L., German Patent 2, 057, 114 of 3 June 1971; *Chem. Abstr.*, 75, 94395f, (1971).
229. Lal, S. and Christian, G. D., *Anal. Chem.*, 43, 410 (1971).
230. Lal, S., *Fresnius' Z. Anal. Chem.* 255(3), 210 (1971).
231. Lal, S., *Fresenius' Z. Anal. Chem.*, 255(3), 209 (1971).
232. Lal, S. and Christian, G. D., *Naturwissenschaften*, 58, 362 (1971).
233. Vanni, A. and Daniele, P. G., *Ann. Chim. (Rome)*, *65(1—2)*, *55* (1975).
234. Starý, J. and Lamm, C. G., *Talanta*, 15, 689 (1968).
235. Cosofret, V. V., *Rev. Chim. (Bucharest)*, 25, 836 (1974).
236. Odajima, O. and Kondo, O., *Japan Patent* 105804, (1975).
237. Grey, P. and Cave, G. C. B., *Can. J. Chem.*, 47(24), 4543 (1969).
238. Agterdenbos, J., Jütte, B. A. H., and Elberse, P. A., *Talanta*, 17, 1085 (1970).
239. Einaga, H., Ishii, H., and Iwasaki, I., *Jpn. Anal.*, 20, 1355 (1971); *Chem. Abstr.*, 76, 54022w, (1972).
240. Ohmacht, R., *Magy. Kem. Foly.*, 82(7), 313 (1976); *Chem. Abstr.*, 86, 37304d, (1977).
241. Fano, V., Licci, F., and Zanotti, L., *Anal. Chim. Acta*, 71, 218 (1974).
242. Vollenweider, M., Danse, A., Summerson, C., Krueger, M., and Stoch, H., *Nat. Inst. Metall., Repub. S. Afr., Rep.*, No. 952, 1970, 1.
243. Sindhwani, S. K. and Singh, R. P., *Fresenius' Z. Anal. Chem.*, 259, 262 (1972).
244. Galík, A., *Talanta*, 16, 201 (1969).
245. McClellan, B. E. and Sabel, P., *Anal. Chem.*, 41, 1077 (1969).
246. Vinokurova, O. B. and Kletenik, Yu. B., *Zh. Anal. Khim.*, 31(6), 1067 (1976); *Chem. Abstr.*, 86 164029x, (1977).
247. Vasil'ev, V. V. and Kabeiya F., *Vestn. Leningr. Univ. Fiz., Khim.*, 1, 146 (1976); *Chem.Abstr.*, 84, 170386g, (1976).