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GAS CHROMATOGRAPHY OF TRANSITION METAL DERIVATIVES OF THE SULPHUR ANALOGUES OF 4,4'-(ETHANE-1,2-DIYLDIIMINO)BIS-(PENT-3-EN-2-ONE)

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SUMMARY

The thermoanalytical and gas chromatographic behaviour of the copper(II), nickel(II), zinc(II), cadmium(II), palladium(II) and platinum(II) chelates of 4,4'-(ethane-1,2-diylldiimino)bis(pent-3-ene-2-thione) and the copper(II) and nickel(II) chelates of 4-[(3-oxo-1-methylbut-1-enyl)aminoethylamino]pent-3-ene-2-thione are reported here for the first time. With the exception of the cadmium chelate, the derivatives elute as sharp, symmetrical peaks at microgram levels without extensive decomposition. Detection limits with flame ionization detection were in the range 0.2-1.5 ng of metal. A nearly complete separation of five chelates of the first ligand is demonstrated. The use of this reagent for the simultaneous determination of copper, nickel and zinc has been examined.

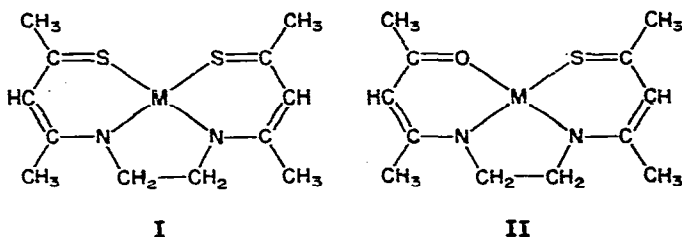
INTRODUCTION

Following the extensive gas chromatographic (GC) studies of metal β -diketonates and their useful but limited applications in quantitative analysis, attention has focussed on the derivatives of other ligands. Among those studied¹ are the chelates of dialkyldithiocarbamic and dialkyldithiophosphoric acids, mono- and dithio- β -diketones, bi- and tetradentate β -keto enamines and salicylaldehydes. These classes of ligands, however, have not been extensively studied and their potential as gas chromatographic reagents has still to be clearly established.

At present, the most promising reagents for analytical purposes, apart from the β -diketones, are the tetradentate β -keto enamines, particularly those with fluoroalkyl substituents such as 1,1,1,1',1',1'-hexafluoro-4,4'-(ethane-1,2-diylldiimino)bis(pent-3-en-2-one). A wide variety of such ligands and their chelates have been prepared and studied by GC¹⁻⁴. The application of these selective reagents has, furthermore,

extended the range of elements determinable at 10^{-9} to 10^{-12} g to include copper, nickel, palladium and vanadium. Their value, thus, is supplementary to the β -diketones which are suited to the determination of elements such as beryllium, aluminium, chromium, cobalt and rhodium. Despite the excellent GC characteristics of the β -keto enamine chelates, relatively little has appeared on analytical applications although several studies⁵⁻⁷ have established the value of these reagents in quantitative trace analysis.

In this paper an assessment of the sulphur-containing ligands 4,4'-(ethane-1,2-diyl-diimino)bis(pent-3-ene-2-thione) and 4-[(3-oxo-1-methylbut-1-enyl)aminoethyl-amino]pent-3-ene-2-thione as GC derivatizing reagents is presented. Their chelates (I and II, respectively) are related to the β -keto enamine derivatives by the replacement of one or both of the oxygen donor atoms with sulphur.



Although tetradentate β -keto enamines have been known for a long time⁸, the analogous β -thiono enamines have only recently⁹⁻¹¹ been prepared. Few of the properties of such compounds and their chelates have been reported and this paper is an initial study of both the thermoanalytical and gas chromatographic properties of chelates of I and II. The potential of the β -thiono enamines lies in their selectivity for derivatives of b-class ions such as palladium(II) and platinum(II) so that this type of ligand may be valuable in the extraction and gas chromatographic determination of these ions. As a group these may also be suitable reagents for zinc(II) and cadmium(II) which cannot at present be determined by GC at the nanogram level.

EXPERIMENTAL

Preparative

The ligands 4,4'-(ethane-1,2-diyl-diimino)bis(pent-3-ene-2-thione), DT-AAED, and 4-[(3-oxo-1-methylbut-1-enyl)aminoethyl-amino]pent-3-ene-2-thione, MT-AAED, were isolated from products of the reaction using 4,4'-(ethane-1,2-diyl-diimino)bis(pent-3-en-2-one), AAED, in a method originally described¹¹ for DT-AAED. The ligands were separated on a column (25 × 5 cm O.D.) of silica gel (Merck type 60 for TLC) using 4-g lots of crude reaction product. DT-AAED was eluted with benzene-ethyl acetate (9:1, v/v) and MT-AAED with benzene-ethyl acetate (1:1, v/v). After removal of solvent each residue was purified by recrystallizing twice from methanol. The ligands are characterized as follows. DT-AAED: bright yellow needles, corrected m.p. 150° (lit.¹¹ 140–141°). C₁₂H₂₀N₂S₂ requires C 56.2, H 7.9, N 10.9, S 25.0%; found: C 56.0, H 7.9, N 10.8, S 24.9%. mol. wt.: calculated 256.4; found 251 (by vapor

pressure osmometry in acetone at 25°). MT-AAED: bright yellow needles, corrected m.p. 112°. $C_{12}H_{20}N_2OS$ requires C 60.0, H 8.4, N 11.7, S 13.3%; found C 60.0, H 8.4, N 11.6, S 13.2%. mol. wt.: calculated 240.0; found 241.

The copper and nickel chelates of AAED and MT-AAED and the zinc, copper, nickel, cadmium and palladium chelates of DT-AAED were prepared and purified by methods similar to those described^{3,10} in the literature. The platinum(II) chelate of DT-AAED, which has not been reported previously, was obtained in less than 10% yield as orange needles (m.p. 348°) by the reaction of potassium tetrachloroplatinate(II) with ligand in methanol. The chelate was separated from other products on a column of silica gel and recrystallized from a mixture of dichloromethane and tetrachloromethane. The copper(II) and nickel(II) chelates of MT-AAED, which also have not been reported previously, were obtained as brown needles (m.p. 188°) and green needles (m.p. 242°), respectively, whereas the zinc(II) derivative could not be obtained using the above methods. The identity of all chelates was confirmed by mass spectrometry and the purity established by analysis for carbon, hydrogen, nitrogen, sulphur and metal content.

Instrumentation

Thermoanalytical data were obtained on a Rigaku Denki Thermoflex Model M8076 combined DTA/TG instrument using a temperature scan rate of 5°/min. A quantity of 7.5 mg of each compound in an aluminium cup was used for each run. Gas flow (nitrogen) through the inner silica furnace tube was fixed at 100 ml/min.

A Varian Model 1700 gas chromatograph equipped with a flame ionization detector (FID) and a Hewlett-Packard 3380A integrator was used. Dry, commercial high-purity nitrogen was employed as carrier gas (30 ml/min). The temperatures of the injection block, column and detector were 240°, 230° and 240°, respectively, unless stated otherwise.

The columns employed were borosilicate glass coils (3 ft. \times $\frac{1}{8}$ in. O.D.) packed with Chromosorb 750 or Gas-Chrom Q (80–100 mesh, AW DMCS) coated with 3% w/w SE-30 and OV-101, respectively. Columns were conditioned for 2 days at 250° then silylated with both HMDS and BSTFA at 180° (200 μ l each) and conditioned at 250° for a further day before use. Chelate solutions were injected onto the columns through a borosilicate glass insert. To minimize interaction of chelate vapors with hot metal surfaces the connection between the column outlet and detector was replaced with one which was glass-lined.

Chelate solutions

Each chelate or ligand (5 mg) was prepared initially in dichloromethane (10 ml) as a 0.05% solution. Further dilution with carbon disulphide provided solutions containing 0.5, 0.05, 0.005 μ g chelate for each injection (1 μ l). Detection limits, tailing indices and calibrations were obtained by making serial injections beginning with the most concentrated solution.

Examination of chelates eluted from the GC column

To determine whether chelates eluting from the column were decomposing at 230° samples were collected at the detector. For this purpose the detector flame was extinguished and the collector (anode) removed. A borosilicate glass tube

(15 cm × 3 mm O.D.) was inserted over the detector jet by means of a PTFE sleeve. The tube, extending above the detector, was cooled with dry-ice pellets. Chelate was injected onto the column (10 × 10 μg) and any condensed material washed into a small vial with several drops of dichloromethane. The solution was examined by chromatography on silica gel layers with ethyl acetate–benzene (1:9, v/v) and by mass spectrometry.

Procedure for simultaneous extraction of zinc, copper and nickel ions as DT-AAED derivatives

A solution containing 10 μg/ml each of zinc, copper and nickel was prepared by dilution of stock solutions (1000 μg/ml). For construction of a calibration curve 0.0, 2.0, 4.0, 8.0 and 10.0-ml aliquots of the substock solution were transferred to 50-ml beakers, evaporated nearly to dryness and treated with 10% (w/v) sodium acetate in methanol (3.0 ml) and 1% (w/v) DT-AAED in acetone (2.0 ml). The solutions were then heated on a hot plate for 20 min at 50° and adjusted to a final volume of 5 ml with methanol. After cooling, distilled water (25 ml) was added and the solutions extracted by shaking for 2 min with carbon disulphide (4.0 ml) containing 0.002% w/v of triacontane as internal standard. Suitable aliquots of "unknown" solutions were processed using the same procedure. Extracts were analysed directly by gas chromatography at 230° on a column of 3% OV-101 on Gas-Chrom Q.

RESULTS AND DISCUSSION

Thermoanalytical properties

The characteristic feature of MT-AAED, DT-AAED and several of their chelates was a low thermal stability suggesting that such compounds were not suitable for GC. In contrast to AAED, for example, which volatilizes without appreciable decomposition³ at temperatures above 300°, MT-AAED and DT-AAED decomposed

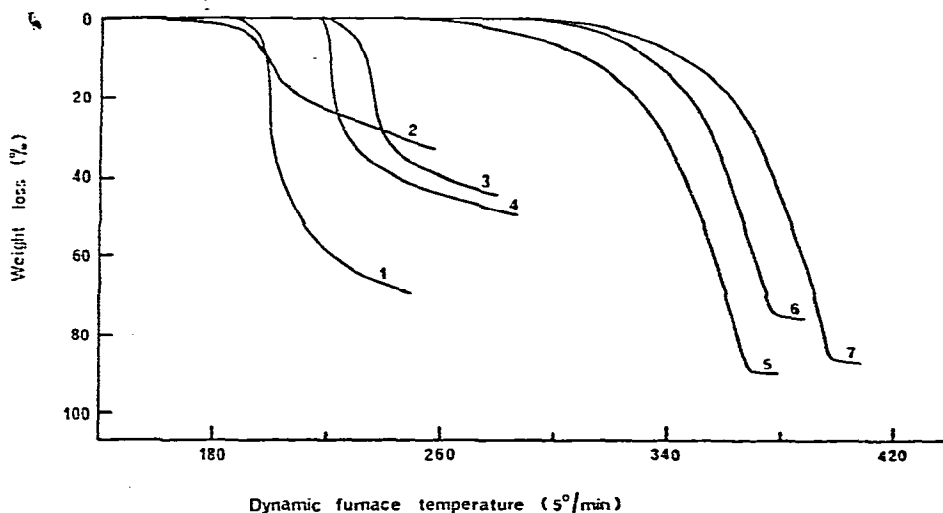


Fig. 1. Thermogravimetric curves for DT-AAED (1) and its chelates with Cd(II) (2), Zn(II) (3), Cu(I) (4), Ni(II) (5), Pd(II) (6) and Pt(II) (7).

exothermally at 212° and 198°, respectively, without volatilizing. From the thermo-analytical data in Fig. 1 and Table I, it is evident that the DT-AAED compounds examined fall into two distinct groups with respect to thermal stability. In the first, the nickel, palladium and platinum chelates are stable to 300° whereas in the second group, the free ligand and the zinc, cadmium and copper chelates are considerably less stable and decompose exothermally at temperatures in the range 185–200°. In the latter group, the chelates decompose on heating to give volatile organic products and dark solids as residues. Above 300° the nickel, palladium and platinum chelates give orange or red-orange sublimates which do not resemble the original compounds. Examination of these sublimates on silica gel layers revealed that, in addition to predominantly undecomposed chelate, an intense red band was also obtained in each case. Mass spectral examination of this band after isolation from silica gel layers showed no evidence of dehydrogenated chelate^{3,12} but contained organic pyrolysis products* whose identity could not be readily established.

TABLE I

PHYSICAL AND CHEMICAL TRANSFORMATIONS IDENTIFIED BY DTA

Abbreviations: f = fusion; v = volatilization; d = decomposition; exo = exothermic; endo = endothermic.

<i>Compound</i>	<i>Temperature (°C)</i>
MT-AAED	113f, 212 d (endo)
Copper chelate	188f, 235 d (exo)
Nickel chelate	242f, 240–310 (v)
DT-AAED	154f, 198 d (exo), 200 d (endo)
Copper chelate	187? 198f, 220 d (exo), 224 d (endo)
Nickel chelate	265f, 260–370 v (d)
Zinc chelate	236 d (exo)
Cadmium chelate	187 d (exo)
Palladium chelate	316f, 300–380 v (d)
Platinum chelate	348f, 320–400 v (d)

The contrast in thermal stabilities suggests a fundamental difference in the chemical bonding of the two groups and this, in turn, may be related to differences in the nature of the sulphur–metal σ and d_{π} – d'_{π} bonds. Features which may serve to lower thermal stability in chelates or ligands containing sulphur in place of oxygen are the greater size and polarizability¹³ of the former. Thus, due to its greater nucleophilic character compared to oxygen, sulphur may more readily initiate pyrolytic decomposition in compounds. In addition, sulphur forms extraordinarily stable sulphides with b-class metal ions, which may be produced when the chelates are heated to high temperatures. Evidence for the production of sulphides in DT-AAED and its copper, zinc and cadmium chelates is suggested in the highly exothermic nature of the

* As an example, in the platinum chelate of DT-AAED the extract of the red band gave a mass spectrum with intense peaks at m/z 306, 223, 206, 149 and 91, absent in the spectrum of the pure chelate. Since these peaks did not have an isotopic pattern suggesting the presence of platinum these must be due to organic degradation products.

decompositions. In contrast, MT-AAED, which contains only one sulphur atom per molecule, decomposes endothermally although its copper chelate decomposes exothermally (see Table I). Similar highly exothermic decompositions have been observed with certain β -keto enamine chelates³ in which the β -diketone moiety contains halogen substituents in the α -positions, and in monothio β -diketonates^{14,15}. In these compounds decomposition also appears to be initiated by elimination of a very stable compound. For the nickel, palladium and platinum DT-AAED chelates stabilization may result¹³ from strong sulphur-metal bonding due largely to enhanced $d_{\pi}-d'\pi$ bonding which could lower the tendency for the formation of metal sulphides and decrease the likelihood of decomposition. These chelates, in fact, do not undergo exothermic decompositions although some decomposition occurs during volatilization, albeit at temperatures above 300°.

Assuming a lower dipole moment for the sulphur-containing chelates it can be anticipated that replacement of sulphur for oxygen in AAED would enhance the volatility of the corresponding chelates of MT-AAED and DT-AAED. However, as is clearly shown in Fig. 2, the reverse trend was obtained in the case of the nickel chelates. Furthermore, volatility decreases stepwise as the number of sulphur atoms in the chelate increases. Comparative data for other chelates containing sulphur is not available although evidence¹ suggests that a similar trend occurs in derivatives of mono- and dithio- β -diketones. Since the chelates cannot depart greatly from a square-planar geometry, it is possible to explain volatility effects largely in terms of the high polarizability of the sulphur atom. Sulphur can directly affect chelate volatility by participating in intermolecular metal-sulphur interactions similar to the metal-oxygen interactions previously³ invoked. Moreover, it may also increase electron density in the π -resonance systems of the chelate rings and thereby increase overall polarizability in the chelate molecules and lower volatility. Such considerations suggest that bulky or electron-withdrawing substituents in the chelate would give derivatives of greater volatility more suited to GC.

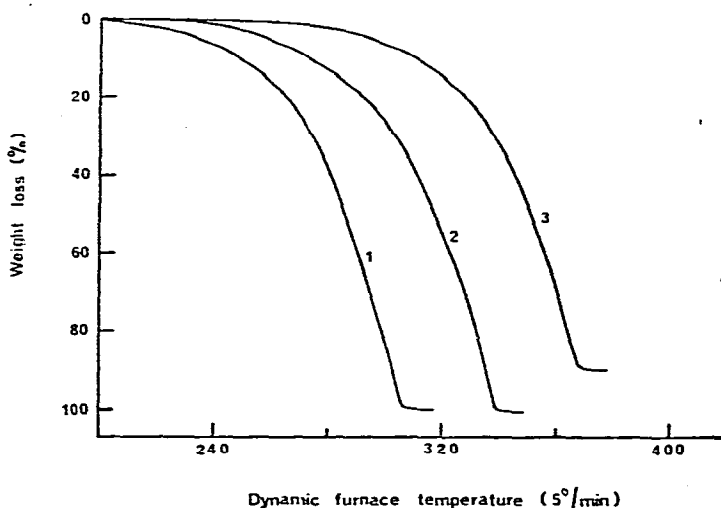


Fig. 2. Thermogravimetric curves for the Ni(II) chelate of AAED (1), MT-AAED (2) and DT-AAED (3).

Gas chromatographic behaviour

In addition to a lower volatility, the thio-chelates had greater retention on SE-30 than the corresponding AAED derivatives. The relative retention of the copper and nickel chelates of the three ligands is shown in Fig. 3. For the DT-AAED chelates column temperatures of 230–240° were generally required to maintain retention times below 20 min. At such temperatures, although rapid decomposition was expected for the less stable derivatives (see Table I), the zinc, copper, nickel, palladium and platinum chelates of DT-AAED eluted from the column without apparent decomposition. As is shown in Fig. 4a, the peaks at the 5- μ g level were relatively sharp and had minimal tailing. Nearly complete separation of the five chelates was obtained on SE-30, however, the copper and nickel chelates were only partly resolved ($R = 0.7$) on this stationary phase. In the case of the cadmium chelate (see Fig. 5) decomposition was evident from the chromatogram. The broad double peak obtained for this compound indicated that an on-column reaction was occurring during its elution.

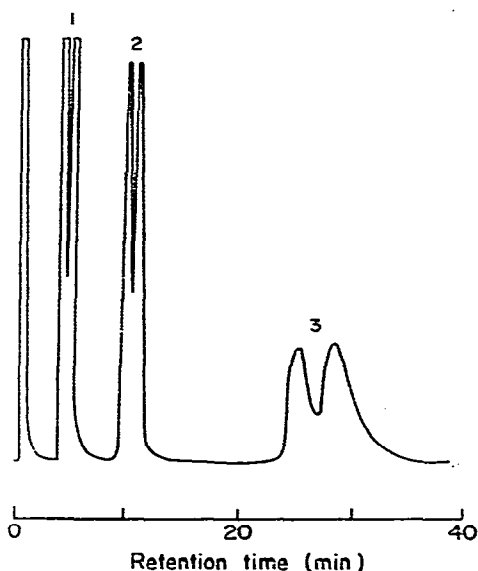


Fig. 3. Chromatogram of a mixture of the Cu(II) and Ni(II) chelates of AAED (1), MT-AAED (2) and DT-AAED (3). For each ligand the copper derivative elutes in advance of the correspondingly nickel(II) derivative. Column, 3% SE-30 on Chromosorb 750; column temperature, 220°.

The reactive nature of the chelates was revealed in their gas chromatographic behaviour. Although several columns gave sharp, symmetrical peaks others, inexplicably, gave broadened, tailing peaks. The repeated introduction of palladium or platinum chelates onto the column also caused a gradual deterioration in the shape and resolution of the peaks as illustrated in Fig. 4b. Furthermore, this deterioration appeared to be irreversible since improvement could not be achieved by re-silylation and conditioning at high temperature. In one instance, the injection of small quantities of crude extract of a platinum chelate permanently destroyed the quality of the column. This behaviour, which has serious implications for possible analytical applications, can be interpreted in terms of decomposition of the chelates to metallic palladium or

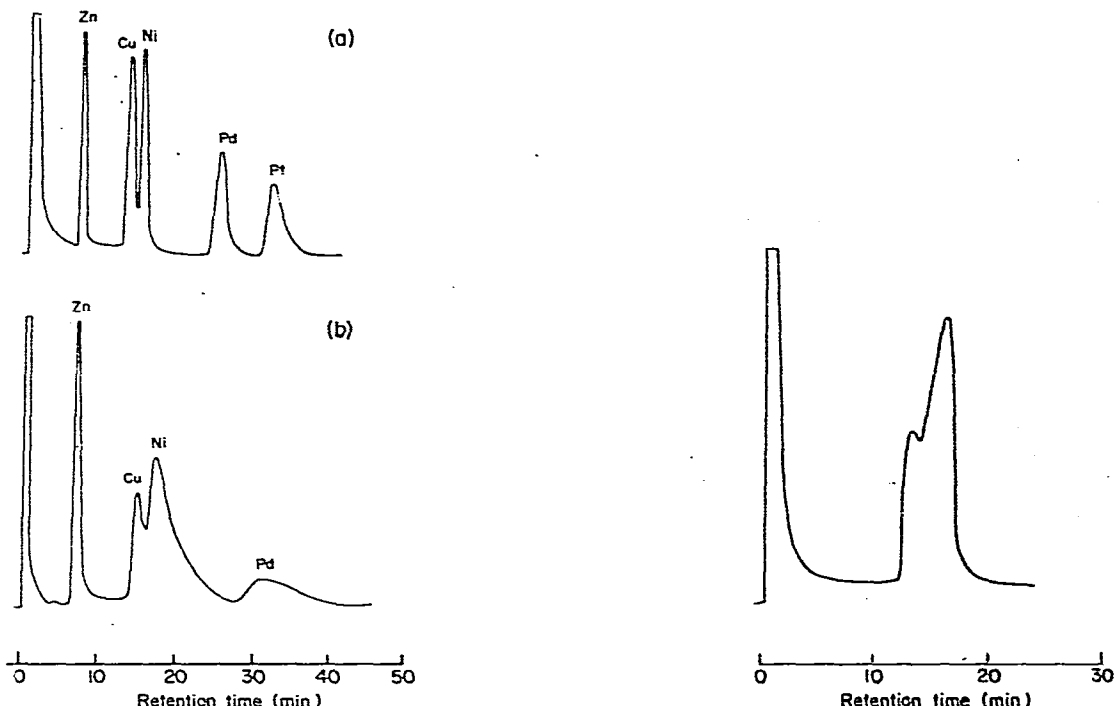


Fig. 4. Chromatogram of a mixture of the Zn(II), Cu(II), Ni(II), Pd(II) and Pt(II) chelates of DT-AAED. a, Obtained on a fresh column; b, the irreversible deterioration in peak shapes resulting from the introduction of palladium or platinum chelates onto the column. Column, 3% SE-30 on Chromosorb 750; column temperature, 230°.

Fig. 5. Chromatogram of the Cd(II) chelate of DT-AAED. Conditions as in Fig. 4.

platinum which may then catalyse the decomposition of chelates subsequently injected into the column. Indeed, the ability of these metals to promote the dehydrogenation of β -keto enamine chelates has been demonstrated^{3,12} and it is possible that similar reactions occur with the more reactive β -thiono enamine analogues. Consistent with this interpretation when only zinc, copper and nickel chelates were introduced into the columns, no deterioration in the peak shapes was obtained even after extensive use of the column.

Recovery of chelates eluted at 230° established that decomposition occurred to some extent even for the more stable nickel, palladium and platinum chelates. Examination of recovered zinc, copper, nickel, cadmium and palladium chelates on silica gel layers revealed numerous additional compounds. For example, the zinc chelate, normally only a yellow band with R_F 0.45, gave a red band (R_F 0.75), a yellow band (R_F 0.64) and a brown band (R_F 0.0), also. In the mass spectrum of this material intense peaks not present in the spectrum of the pure chelate were observed at m/z 362, 360, 314, 312 and 310.

It was possible to detect nanogram quantities of DT-AAED chelates eluting from the column. Detection limits given in Table II were not limited by adsorption but by the detector noise at high sensitivity, however, a linear response was obtained in the range 5–0.005 μg for each of the chelates in Table II. The degree of peak tailing

depended markedly on the quality of the column but little difference was observed between the various chelates. Tailing indices¹⁶ obtained for the zinc and nickel derivatives with SE-30 on Chromosorb 750 as support are shown in Table III and indicate a considerable degree of tailing at the lower level of 0.05 μg . Little or no tailing was obtained at this level on the column with OV-101 on Gas-Chrom Q and this was used for analytical purposes.

TABLE II

DETECTION LIMITS (FID) FOR CHELATES OF DT-AAED

Detection limits are based on a twice noise level criterion.

Metal	Detection limit (ng)	
	Chelate	Metal
Zinc	5	1
Copper	5	1
Nickel	1	0.2
Palladium	5	1.5

TABLE III

TAILING INDICES FOR THE ZINC AND NICKEL CHELATES OF DT-AAED

Metal	$T_{0.1}^5$	$T_{0.1}^{0.5}$	$T_{0.1}^{0.05}$
Zinc	1.0	1.8	20
Nickel	1.2	6	18

Simultaneous extraction and analysis of zinc, copper and nickel

In ascertaining the feasibility of using GC for determining zinc, copper and nickel simultaneously, solutions containing known concentrations of each metal in the range 10–100 $\mu\text{g}/\text{ml}$ were prepared and analysed following conversion to the DT-AAED derivatives. Derivatization involved reaction of the metal ions with ligand in methanol containing excess sodium acetate. Following the addition of water and extraction with carbon disulphide, the extracts, found to be stable for up to 6 days, were analysed directly by GC (see Fig. 6). Comparison of peak areas obtained for the extracts, with those of solutions of the purified, solid chelates showed that greater than 90% recovery was attained for each ion.

Various difficulties were experienced in the analysis of the metal ions. When the concentrations of the copper and nickel derivatives differed by greater than a factor of about five it became difficult to obtain accurate area measurements for the minor component. Tailing of the ligand peak also interfered with the determination of zinc. This interference appeared difficult to avoid since excess ligand was required to ensure complete derivatization of the ions. Furthermore, unlike many β -diketones, DT-AAED is insufficiently acidic to be removed from the organic extract by washing with aqueous sodium hydroxide. For the chromatogram shown in Fig. 6, ligand concentration 50-fold in excess of the total ion concentration was employed. It is important that the ligand should not exceed 100-fold excess concentration because of the difficulty in measuring the areas of early peaks. At the sensitivity used in the analyses, inter-

ference was also experienced from the tailing peaks of solvents such as dichloromethane, nitromethane and ethyl acetate. To avoid this, it was convenient to use carbon disulphide which gave both a low FID response and satisfactory extraction.

Fig. 7 shows that a linear calibration curve can be obtained in the range 0–25 $\mu\text{g}/\text{ml}$ of metal provided a fresh column was used for each chelate. The concentrations of the metals found by GC shown in Table IV, however, were in poor agreement with the actual concentrations and re-examination of the procedure revealed an unacceptable reproducibility for the copper chelate peak which became more erratic with continued use of the column. Since each concentration was expressed as a percentage of the total peak area, this also probably explains the results obtained for nickel and zinc. As observed also in studies¹⁶ of the fluorinated β -diketonates of oxovanadium(IV), peaks corresponding to the copper derivative were obtained when solutions of the pure ligand were injected onto the column. This clearly suggested that reactions were occurring in the injection port and, indeed, inspection of the column revealed a black deposit on the glass wool plug at the inlet. Evidently the deposit, formed from pyrolysis of the copper chelate, was reacting with excess ligand in the extracts subsequently injected onto the column, regenerating the chelate which then eluted with the analyte to give an erroneous result.

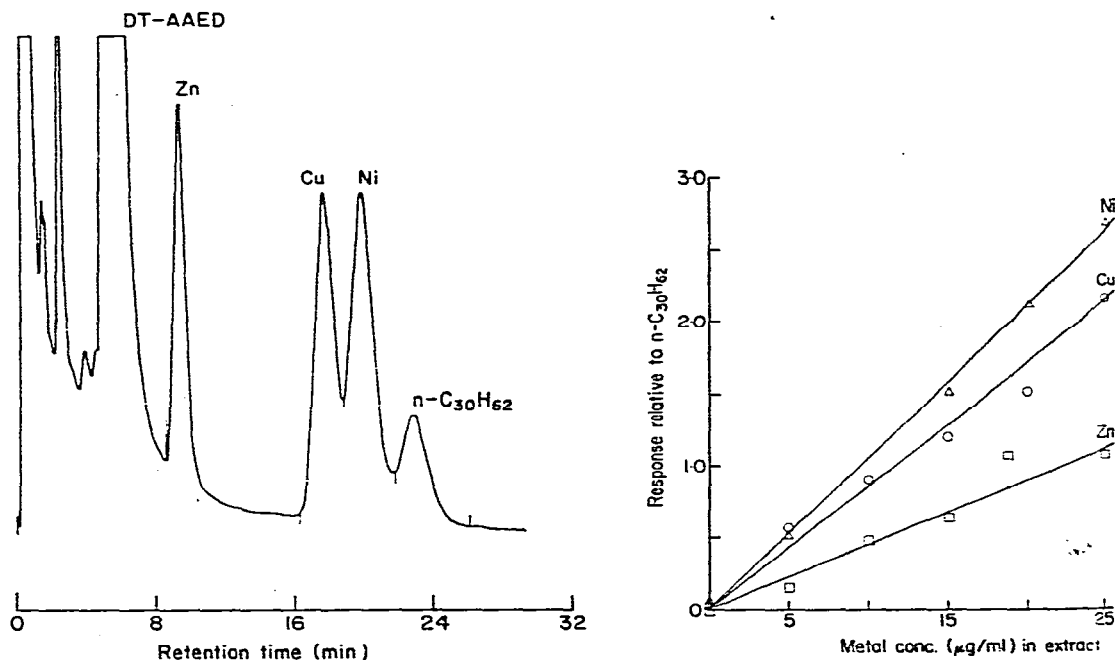


Fig. 6. Chromatogram of the Zn(II), Cu(II) and Ni(II) chelates of DT-AAED following derivatization and extraction with carbon disulphide. Peaks for each chelate correspond approximately to 20 ng of metal. Column 3% OV-101 on Gas-Chrom Q. Conditions as in Fig. 4.

Fig. 7. Calibration curves for zinc, copper and nickel extracted as the DT-AAED derivatives for concentrations in the range 0–25 $\mu\text{g}/\text{ml}$ of each ion in the carbon disulphide extract. Column and conditions as in Fig. 6.

TABLE IV

GAS CHROMATOGRAPHIC ANALYSIS OF SOLUTIONS CONTAINING ZINC, COPPER AND NICKEL IONS

Solution	Actual concn. ($\mu\text{g/ml}$)			Found by GC ($\mu\text{g/ml}$)		
	Zn	Cu	Ni	Zn	Cu	Ni
1	40.0	20.0	20.0	38.6	17.8	27.0
2	20.0	50.0	10.0	23.0	54.8	4.0
3	10.0	30.0	50.0	4.0	20.0	30.0

As this problem is not readily overcome the above procedure cannot, at this stage, be recommended as a practical method for the simultaneous determination of the three metals although it may be useful for the analysis of nickel and zinc in the absence of copper. Moreover, the use of MT-AAED as an alternative reagent whose derivatives are more volatile and elute at lower column temperatures seems handicapped. Like AAED, MT-AAED does not appear to produce a zinc chelate and a peak corresponding to this derivative was not observed in the extracts even through the copper and nickel compounds appeared to elute normally. Currently, investigations of other tetradentate β -thiono enamines are progressing with a view to identifying more suitable reagents.

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