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Short communication

## Gas and liquid chromatography of metal chelates of pentamethylene dithiocarbamate

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### Abstract

Capillary GC and HPLC of metal chelates of pentamethylene dithiocarbamate were examined. Copper(II), nickel(II), cobalt(III), iron(III), manganese(II) and chromium(III) chelates formed in slightly acidic media (pH 5) were extracted in methyl isobutyl ketone or chloroform. Capillary GC elution and separation was carried out on methylsilicone DB-1 column (25 m×0.2 mm I.D.) with film thickness 0.25 μm. Electron-capture detection was used. Elution was carried at initial column temperature 200 °C with an increment at a rate of 5 °C/min up to 250 °C and maximum temperature was maintained for 10 min. Symmetrical peaks with baseline separation were obtained with the metal chelates investigated with linear calibration range between 5 and 25 μg/ml for each metal ion and detection limits in the range of 0.5–6.0 μg/ml corresponding to 27–333 pg of metal ion reaching to the detector. HPLC separation was carried out from LiChrosorb ODS, 5 μm column and complexes eluted with methanol–water–1 mM sodium acetate (70:28:2, v/v) with a flow-rate of 1.2 ml/ml. UV detection was at 260 nm. The detection limits obtained were in the range 2–6 μg/ml. The methods were applied to the determination of metal ions in canal water and coal samples with RSD values within 4.15%. The results when compared with a standard flame atomic absorption spectrophotometric method and revealed no significant difference.

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### 1. Introduction

The analytical procedures for the determinations of metal ions by capillary gas chromatography (cGC) and high-performance liquid chromatography (HPLC) are increasing slowly [1–6]. The GC of metal chelates is restricted to thermally stable and volatile metal chelates of β-diketone, monothioacetylacetones, bi- and tetradentate ketoamine

Schiff bases, dialkyl dithiocarbamate, dialkyl dithiophosphates, and metalloporphyrins [1,2,7–13]. Dithiocarbamates are extensively reported as complexing reagents for the solvent extraction, spectrophotometric and liquid chromatographic determination of metal ions [14–19]. GC of the diethyl dithiocarbamates and trifluoroethyl dithiocarbamate is also possible [20–29]. The reagents have been used for GC separation and determination of metal ions using both packed and capillary columns. The dithiocarbamates most studied for HPLC are different dialkyl dithiocarbamate [30], pyrrolidine dithio-

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carbamate [31], bis(2-hydroxyethyl) dithiocarbamate [32], hexamethylene dithiocarbamate [33] and dibenzyl dithiocarbamate [34].

Pentamethylene dithiocarbamate (piperidine dithiocarbamate) (PMDTC) has been reported as complexing reagent for the solvent extraction and determination of Fe, Ni, Cr and Mn using flame atomic absorption spectrometry (FAAS) [35]. The reagent has also been used for the determination of cadmium(II), copper(II), iron(III) and lead(II) on thin-layer chromatography [36]. The present work examines PMDTC for the separation and determination of copper(II), nickel(II), chromium(III), cobalt(III), iron(III) and manganese(II) using capillary GC and reversed-phase HPLC. It is also intended to extend the applications of dithiocarbamates for chromatographic determination of metal ions.

## 2. Experimental

### 2.1. Preparation of the reagent

The sodium salt of PMDTC was prepared as reported [35]. Carbon disulfide (15.2 g, 0.2 M) was slowly added with constant stirring to freshly distilled piperidine (16.8 g, 0.2 M) dissolved in 25 ml of water at  $>5^{\circ}\text{C}$ , sodium hydroxide (8 g) dissolved in 10 ml of water was then added. The precipitate obtained was filtered and recrystallized from chloroform. Freshly prepared 100 ml, 1% reagent solution in water was shaken with 5 ml of methyl isobutyl ketone (MIBK). The aqueous phase was collected and kept at  $4^{\circ}\text{C}$  when not in use. Fresh solution was prepared every week.

### 2.2. Analytical procedure for capillary GC

Solution (1–2 ml) containing copper(II), nickel(II), iron(III), chromium(III) and cobalt(III) (10–50  $\mu\text{g}$ ) each was added PMDTC reagent (1%, w/v, 1 ml), sodium acetate–acetic acid buffer pH,  $5.0 \pm 0.5$  (1 ml), and 1 ml MIBK. The contents were mixed well and layers were allowed to separate. The organic layer was collected and extraction was repeated with 1 ml of MIBK. The final volume was adjusted to 2 ml. The solution (1  $\mu\text{l}$ ) was injected on the capillary column DB-1 (25 m  $\times$  0.2 mm I.D.) with

layer thickness 0.25  $\mu\text{m}$  at initial column temperature  $200^{\circ}\text{C}$  with programmed rate of increase in temperature  $5^{\circ}\text{C}/\text{min}$  up to  $250^{\circ}\text{C}$ . Maximum temperature was maintained for 10 min. Helium gas flow-rate was 3.5 ml/min with split ratio 1:18. The detector and injector temperatures were fixed at 260 and  $270^{\circ}\text{C}$ , respectively. An electron-capture detection (ECD) system was used.

### 2.3. Analytical procedure for HPLC

To 1–2 ml solution containing chromium(III), manganese(II), iron(III), cobalt(III), nickel(II) and copper(II) between 8 and 100  $\mu\text{g}$  was added 1 ml of sodium acetate buffer, pH 5.0, 1 ml PMDTC (1%, w/v) and 1 ml of chloroform. The contents were mixed well and layers were allowed to separate. The final volume was adjusted to 2 ml. The solution (20  $\mu\text{l}$ ) was injected on LiChrosorb ODS, 5  $\mu\text{m}$ , column (150  $\times$  4.6 mm I.D.) and complexes eluted with methanol–water–1 mM sodium acetate (70:28:02, v/v) with a flow-rate of 1.2 ml/min and UV detection at 260 nm.

### 2.4. cGC determination of copper(II), nickel(II), iron(III), manganese(II) and chromium(III) from canal water

Fuleli canal takes off from left bank of river Indus at Kotri Barrage and passes through Hyderabad City (Pakistan), where untreated and partially treated city sewage is added. Four water samples were collected from Hyderabad City, (1) near the Sabzazar restaurant, (2) near the Government College, Hyderabad, after the addition of sewage water, (3) before railway line crossing and (4) after railway line crossing, after addition of sewage water. Water samples were collected from the surface of water within 30 cm. Water samples were filtered through Whatman 42 filter paper and filtrate (250 ml) was transferred to separating funnel. Sodium acetate–acetic acid buffer pH 5.0 (5 ml), reagent PMDTC (5 ml, 1%, w/v) and MIBK solvent 2–3 ml were added. The contents were mixed well and layers were allowed to separate. The organic layer was separated and extraction was repeated with 2 ml of MIBK. The final volume was adjusted to 5 ml with MIBK. Capillary GC elution was carried out as described in Section 2.2.

The detection was by ECD. Quantitation was by external calibration curve prepared by adding known amount of metal ions to 250 ml of double distilled water and following the above extraction procedure. The blank was also prepared simultaneously using 250 ml of double-distilled water.

### 2.5. HPLC analysis of coal samples

Coal sample was collected from Lakhra coal mines (Sindh, Pakistan) and after crushing, mixing and subdividing; a 5-g sample was weighed and transferred to a beaker. Nitric acid (10 ml, 65%) and hydrochloric acid (10 ml, 37%) were added and heated gently. More nitric acid (10 ml, 65%) was added to complete dissolution. Finally 5 ml of hydrochloric acid was added and heated to near dryness. The residue was dissolved in water and filtered through Whatman 42 filter paper. The final volume was adjusted to 50 ml. The pH of 1 ml solution was adjusted to 5 and the analytical procedure in Section 2.3 was followed. The amount of chromium, manganese, iron, cobalt, nickel and copper were evaluated from external calibration curve.

### 2.6. Metal analysis by FAAS

Water sample (1) collected near the Sabzazar Restaurant was analyzed for metal contents as under. Water sample was filtered and sample 250 ml was heated gently (90 °C) to about 5 ml. The final volume was made up to 10 ml and analyzed by FAAS analyses were carried out on a Varian spectra atomic absorption spectrophotometer using air acetylene and nitrous oxide–acetylene flame at the conditions recommended by manufacturer. The determination of Cr, Mn, Fe, Co, Ni, and Cu in coal samples after acid digestion was also carried out using flame AAS. Analysis was carried out in triplicate with integration time 3 s and delay time 3 s. Redistilled methanol (G.R. grade), acetonitrile, sodium acetate, nitric acid (65%) hydrochloric and (37%), chloroform, carbon tetrachloride, carbon disulphide and pipridine of E Merck (Darmstadt, Germany) were used. Freshly prepared and deaerated double-distilled water was used for HPLC studies.

Solution containing 1 mg/ml of copper(II), nic-

kel(II), chromium(III), iron(III), cobalt(III) and manganese(II) were prepared from copper(II) nitrate, nickel(II) chloride, chromium(III) chloride hexahydrate, ammonium iron(III) sulfate hexahydrate, cobaltous nitrate hexahydrate and manganese chloride tetrahydrate, respectively, of E. Merck. The solutions of lower concentration were prepared by an appropriate dilution.

Buffer solutions at unit interval within pH 1–9 were prepared from the following: hydrochloric acid (0.1 M), potassium chloride (1 M), acetic acid (1 M), sodium acetate (1 M), ammonium acetate (1 M) ammonia (1 M), sodium hydrogen-carbonate (1 M) and sodium carbonate (saturated). All pH measurements were made with an Orion 420A pH meter. GC studies were carried out with a Perkin-Elmer 8700 gas chromatograph with a split/splitless injector, flame ionization detection (FID) or  $^{63}\text{Ni}$  ECD as detection system and an Epson LX-800 printer. Pure nitrogen and helium gases were obtained from Pakistan Oxygen, Karachi. Hydrogen gas and air for FID were from a Shimadzu OPGU-i500S hydrogen generator and a Hitachi Bebigon air compressor. Capillary column poly(dimethylsilicone), SGE, Australia (25 m×0.2 mm I.D.) with 0.25  $\mu\text{m}$  film thickness was used throughout the study. IR of the reagent PMDTC in KBr was carried out on Hitachi Model 260-50 IR spectrophotometer.

A Hitachi model 6400 liquid chromatograph connected with variable wavelength UV spectrophotometric detector, LiChrosorb ODS, 5  $\mu\text{m}$  column (150×4.6 mm I.D.) (E. Merck), Rheodyne 7125 injector and Hitachi D-2500 Chromato-integrator were used.

## 3. Results and discussion

The reagent PMDT reacts with metal ions in aqueous–ethanolic solution in slightly acidic to neutral solution to form metal chelates (Fig. 1). The

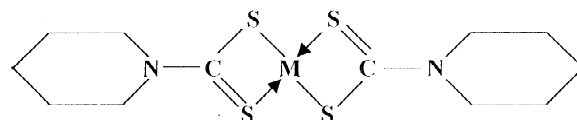


Fig. 1. Structural diagram of PMDTC–metal complex.

complexes are extractable in non-aqueous media. The elution and separation of the metal chelates of PMDTC from the methylsilicon CGC column were examined. The complexes eluted as single peak and separated completely from derivatizing reagent. The optimal separation between copper(II), nickel(II), cobalt(III), iron(III), chromium(III) and manganese(II) complexes was obtained with initial column temperature of 200 °C with programmed rise in temperature of 5 °C/min up to 250 °C and maximum temperature for 10 min. Helium flow-rate was 3.5 ml/min and split ratio 1:18. Total analysis time was less than 14 min. The resolution factor ( $R_s$ ) between two adjacent peaks was obtained  $>4$  with order of

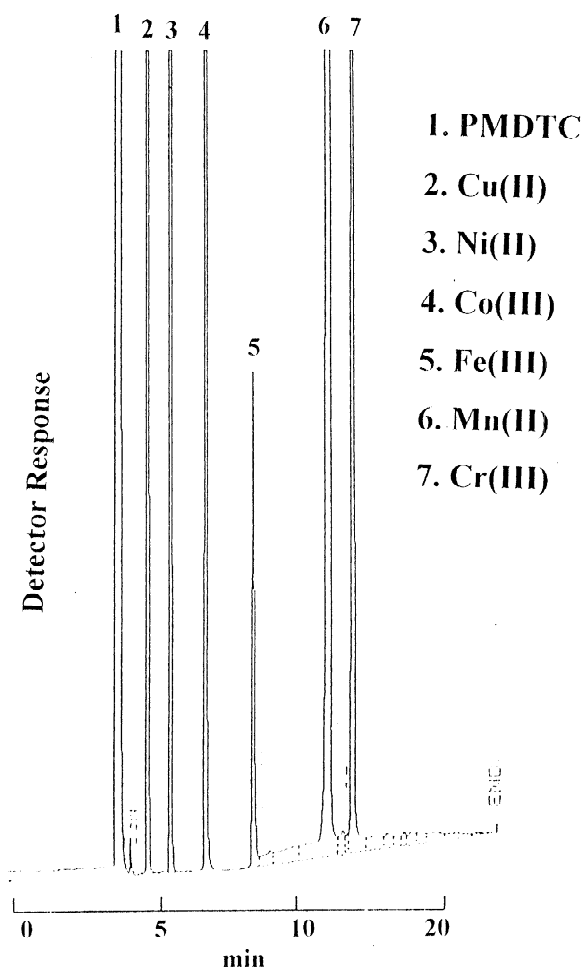


Fig. 2. cGC separation of PMDTC-metal complexes. For conditions see Section 2.2.

elution in sequence of copper(II), nickel(II), cobalt(III), iron(III), manganese(II) and chromium(III) (Fig. 2). The detection was by ECD). Effects of pH, reagent concentration and choice of extracting solvent on the formation and extraction of metal chelates were examined. The average peak area ( $n=3$ ) of each of the complex was measured and the condition which gave maximum response was selected. The pH was varied between 1 and 9 at unit interval, reagent concentration was varied between 0.5 and 3.0 ml of 1% (w/v) solution and extracting solvents MIBK, cyclohexane and *n*-hexane were examined.

A similar response was obtained within pH 4–6 and pH 5 was selected. The reagent concentration 1 ml of 1% and MIBK proved optimal for CGC determination. Using the condition linear calibration curves were obtained by plotting average peak area ( $n=3$ ) versus concentration in the range of 5–25  $\mu\text{g/ml}$  for each of metal ion. The regression coefficients ( $r$ ) were in the range of 0.996–0.999. The calibration ranges corresponded to 0.27–1.35 ng of metal ion reaching to the detector. The detection limits measured as three times the background noise for copper(II), nickel(II), cobalt(III), iron(III), manganese(II) and chromium(III) were 0.5, 2.5, 0.7, 2.5, 4.0 and 6.0  $\mu\text{g/ml}$  corresponding to 27.7, 138.8, 38.9, 138.8, 222.2 and 333.3 pg reaching to the detector. The reproducibility for the determination of 15  $\mu\text{g/ml}$  ( $n=5$ ) was observed with a RSD within  $\pm 4.12\%$ .

Capillary GC indicated complete separation between the metal chelates with acceptable sensitivity in ECD, but for comparative study and for simultaneous determination of the metal ions at trace levels reversed-phase HPLC was also examined. All the complexes after their formation in slightly acidic medium (pH 5) and extraction in chloroform, were injected on LiChrosorb ODS column and complexes were eluted with binary mixtures of methanol–water. All the complexes eluted as symmetric peaks and separated from the excess of derivatizing reagent. Organic solvents chloroform, carbon tetrachloride and MIBK were examined for the ease of quantitative extraction of metal chelates and chloroform gave better results and was used for HPLC studies. The solution stability in chloroform of copper(II), nickel(II), manganese(II), cobalt(III), iron(III) and

chromium(III) complexes were examined. The complex after preparation was injected on the column and average response ( $n=3$ ) was recorded. The complexes were again injected after the different times. The change in an average response more than 5% was considered as an evidence for the change in solution stability. The solution stability of copper(II), nickel(II), manganese(II), cobalt(III), iron(III) and chromium(III) were observed >12, >12, >6, >9 >5, >3 h, respectively.

The separations of metal chelates were next examined using the binary mixture of methanol and water (80:20, v/v), simultaneous separation of all the above metal ions could not be achieved. However,

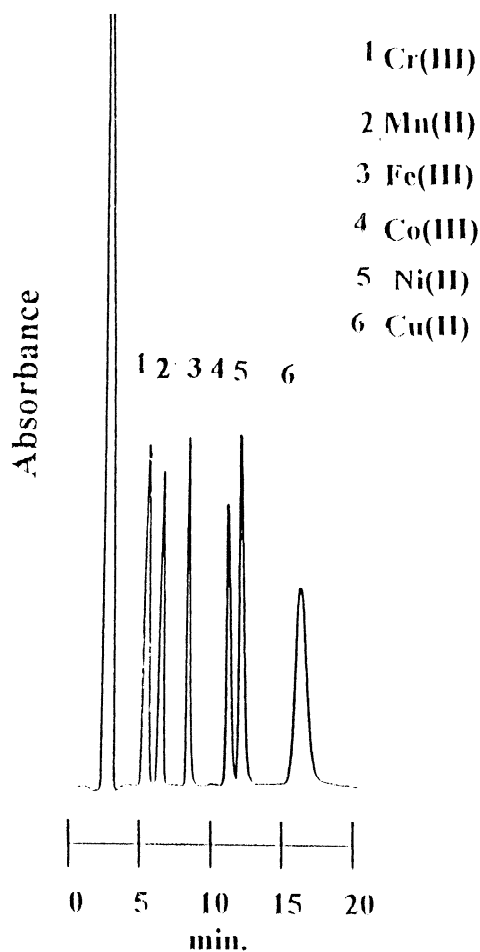


Fig. 3. RP-HPLC separation of PMDTC complexes of Cr(III), Mn(II), Fe(III), Co(III), Ni(II) and Cu(II). For conditions see Section 2.3.

when two LiChrosorb columns (150×4.6 mm I.D) were coupled, an improvement in the separation of manganese(II), iron(III), cobalt(III) and copper(II) was obtained. Optimal separation between chromium(III), manganese(II), iron(III), cobalt(III), nickel(II) and copper(II) was obtained with a mixture of methanol–water–sodium acetate as mobile phase (Fig. 3). Linear calibration curves were ob-

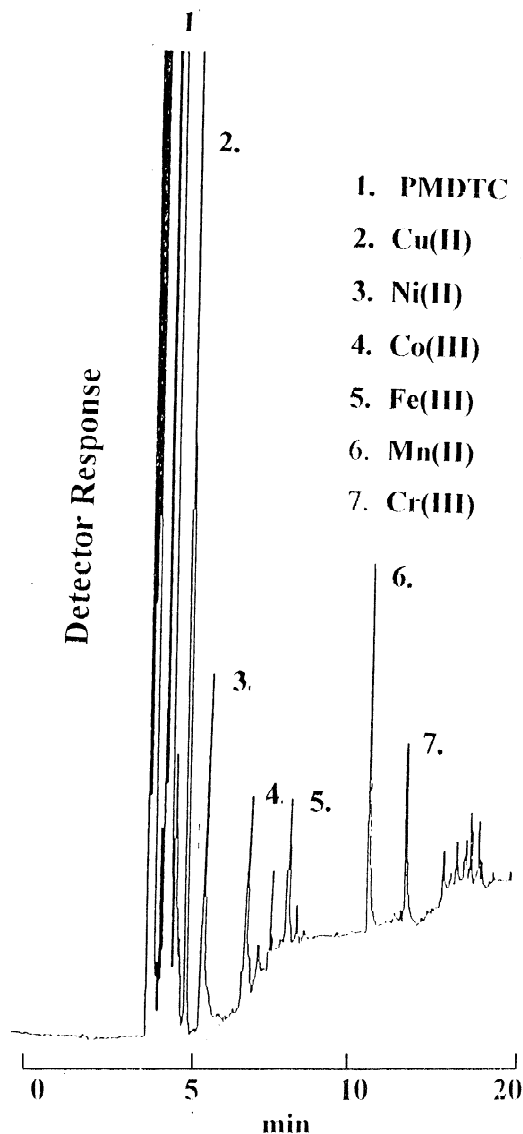


Fig. 4. cGC simultaneous analysis of PMDTC complexes of copper(II), nickel(II), cobalt(III), iron(III), manganese(II) and chromium(III) in canal water. Conditions as in Section 2.

Table 1

cGC analysis of copper(II), nickel(II), cobalt(III), iron(III), manganese(II) and chromium(III) in Fullali Canal water samples: average results ( $n=3$ ) with  $\pm$  confidence interval at 95%

Metal	Concentration ( $\mu\text{g/l}$ )			
	1	2	3	4
Cr(III)	23.38 $\pm$ 3.21 22.87 $\pm$ 6.66*	32.20 $\pm$ 3.88	42.52 $\pm$ 3.72	84.71 $\pm$ 4.70
Mn(II)	16.88 $\pm$ 3.89 15.94 $\pm$ 3.23*	55.45 $\pm$ 3.45	112.82 $\pm$ 3.48	149.52 $\pm$ 3.58
Fe(III)	182.24 $\pm$ 6.22 180.99 $\pm$ 11.34*	210.16 $\pm$ 5.88	317.26 $\pm$ 6.23	363.46 $\pm$ 7.23
Co(III)	19.16 $\pm$ 1.78 21.28 $\pm$ 4.50*	18.02 $\pm$ 1.65	32.45 $\pm$ 2.62	52.05 $\pm$ 3.62
Ni(II)	34.22 $\pm$ 0.82 34.20 $\pm$ 3.52*	41.28 $\pm$ 1.52	62.11 $\pm$ 2.18	71.18 $\pm$ 2.88
Cu(II)	45.22 $\pm$ 1.12 46.22 $\pm$ 4.52*	72.28 $\pm$ 2.18	88.22 $\pm$ 3.21	92.12 $\pm$ 3.28

Analysis by FAAS. Fullali Canal: (1) near the Sabzazar Restaurant; (2) near Government College; (3,4) near Railway Crossing before and after addition of sewage water, respectively.

tained by recording average peak area ( $n=3$ ) versus concentration of each metal ion and were recorded with 4–50  $\mu\text{g/ml}$  for manganese(II), copper(II), nickel(II) and chromium(III) and 5–100  $\mu\text{g/ml}$  for cobalt(III) and iron(III). The coefficient of correlation  $r$  for ( $n=5$ ) point calibration were obtained for chromium(III), manganese(II), iron(III), cobalt(III), nickel(II) and copper(II) 0.995, 0.997, 0.999, 0.996, 0.998 and 0.999, respectively. The detection limits obtained were: iron(III) 2.5, cobalt(III) 3.0, copper(II) 2.0, chromium(III) 6.0, manganese(II) 4.0 and nickel(II) 2.0  $\mu\text{g/ml}$ . The relative standard deviation (RSD) obtained were in the range for chromium(III) 1.34–3.82% manganese(II) 1.12–1.18%, iron(III) 0.8–12%, cobalt(III) 4.6–6.4%, nickel(II) 2.27–4.16 and copper(II) 5.2–5.4%.

### 3.1. Applications

The reagent PMDTC was used for the CGC determination of metal contents in water. The water samples were collected from a canal. The metal contents were determined after pre-concentration by solvent extraction by a factor of 50. The results of metal analysis with confidence interval at 95% are summarized in Table 1. Representative chromatogram for the analysis of a sample is shown in Fig. 4.

Table 2

Determination of metal ions in coal sample by reversed-phase HPLC and FAAS. Average results ( $n=3$ ) with  $\pm$  confidence interval at 95%

Metals	Concentration ( $\mu\text{g/g}$ )	
	RP-HPLC	FAAS
Cr	11.32 $\pm$ 1.08	11.81 $\pm$ 3.27
Mn	7.84 $\pm$ 0.42	8.38 $\pm$ 0.97
Fe	210.0 $\pm$ 2.20	215.90 $\pm$ 7.78
Co	62.78 $\pm$ 0.82	63.08 $\pm$ 4.80
Ni	54.46 $\pm$ 1.16	56.52 $\pm$ 4.482
Cu	182.55 $\pm$ 3.38	180.03 $\pm$ 8.48

The values for metal analysis for samples 2 and 4 are higher as compared to 1 and 3 and are due to the addition of sewage water. The sample 1 after pre-concentration by evaporation was also analyzed by FAAS and a good correlation was obtained with capillary GC procedure. The analysis of coal by HPLC enabled to determine Cr, Mn, Fe, Co, Ni and Cu and results compared well with FAAS (Table 2).

## 4. Conclusion

Capillary gas chromatographic and reversed phase HPLC separation of PMDTC metal complexes (cop-

per(II), nickel(II), cobalt(III), iron(III), manganese(II) and chromium(III) were obtained. The metal complexes were well resolved with a detection limit at picogram level. The methods were applied successfully for the analysis of metal ions in water and coal samples.

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