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Paper Chromatographic Separation of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) & Zn(II) with Solvents Containing Diphenyl Sulphoxide

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Paper chromatographic separation of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) on pretreated papers is studied in the presence of diphenyl sulphoxide in four different solvent systems containing mixtures of 9M HCl, *n*-butanol, isopropanol and acetone. In most of the cases a neat separation has been obtained.

MARKL and Jettmar have reported the extraction of metal cations by reversed phase paper chromatography using diphenyl sulphoxide-HCl and dibenzyl sulphoxide-HCl systems¹. As DPSO has not been used for the extraction of metal ions on

papers impregnated with inorganic ion-exchangers, it is proposed to study the chromatography of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) on papers impregnated with liquid paraffin, zirconium phosphate and tungstate using DPSO in different solvent systems.

Chromatography was performed on Whatman No. 1 paper strips (18×2.5 cm) in glass jars (20×4.5 cm). Metal chlorides and solvents were either of Analar grade or reagent grade and used as such. DPSO was prepared by the method of Shriner². Impregnated papers were prepared by the methods already reported³. Approximately 0.06M solution of metal ions were prepared by dissolving the metal chlorides in 95% ethanol.

Cu(II), Co(II) and Ni(II) were identified by spraying with 0.1% alcoholic solution of rubeanic acid and exposing to vapours of ammonia⁴. Cu(II), Co(II) and Ni(II) gave olive green, yellow and bright blue spots respectively. In the case of untreated papers Zn(II) and Mn(II) gave fluorescent yellow and brown spots respectively when exposed to UV light⁵. In the case of treated papers K₃Fe(CN)₆ was used as a detecting agent⁶. Zn(II) and Mn(II) gave yellow and brown spots respectively. Fe(III) was detected by spraying with KCNS solution which gave blood red spot.

The *R_f* values of the cations were calculated for the following solvent systems:

- 9M HCl+*n*-butanol+acetone (1:1:3, v/v)
- 9M HCl+*n*-butanol+acetone (1:1:3, v/v) + 2% DPSO
- 9M HCl+isopropanol+acetone (1:1:1, v/v)
- 9M HCl+isopropanol+acetone (1:1:1, v/v) + 2% DPSO

In order to prove that DPSO affects the *R_f* values of the cations, they were calculated on plain as well as impregnated papers in the above solvent systems with and without DPSO. Only the solvent mixtures that gave the best results are reported in Table 1.

The results in Table 1 reveal that DPSO affects the *R_f* values of the cations. It is due to the equilibrium established between the chloride and DPSO ligands for the solvation of metal cations. For plain papers, the *R_f* values of cations depend on their partition between the mobile phase and the stationary phase. For papers impregnated with the ion exchangers, the separations depend not only on partition but also on selectivities shown by the ion exchangers for various cations⁷. It has been proved that dried (but hydrous) precipitates of

TABLE 1 — *R_f* VALUES OF SOME CATIONS IN DIFFERENT SOLVENT SYSTEMS

Cation	A		B		C		D		
	Solvent systems*	(i)	(ii)	(i)	(ii)	(iii)	(iv)	(iii)	(iv)
Mn(II)		0.42	0.40	0.40	0.35	0.51	0.43	0.37	0.62
Fe(III)		1.00	0.98	1.00	0.85	1.00	0.88	1.00	0.98
Co(II)		0.79	0.71	0.83	0.50	0.75	0.61	0.77	0.66
Ni(II)		0.12	0.09	0.20	0.24	0.38	0.20	0.17	0.50
Cu(II)		0.92	0.83	0.77	0.59	0.77	0.81	0.74	0.78
Zn(II)		0.97	0.94	0.91	0.83	0.98	0.96	0.97	0.94

A, *R_f* on plain paper; B, *R_f* on paper impregnated with zirconium phosphate; C, *R_f* on paper impregnated with zirconium tungstate; D, *R_f* on paper impregnated with liquid paraffin.

*See text.

Zr(IV) with polyvalent inorganic anions, such as phosphates, tungstates, etc., have useful cation exchange properties including high uptakes of certain ions, reasonable exchange rates and interesting selectivities⁸. DPSO seems to influence the partition affecting the R_f values even on impregnated papers. Paraffin coated papers demonstrate separation of cations by reversed phase chromatography.

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Spectrophotometric Determination of Ru(III) with Promazine Hydrochloride

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Promazine hydrochloride (PMH) is proposed as a new reagent for the spectrophotometric determination of Ru(III) based on the formation of a red-coloured complex in sulphuric acid medium (1.25-2.0M). A twenty-nine-fold molar concentration of the reagent is necessary for the full development of the colour intensity. Beer's law is obeyed for 0.2-11.94 ppm of Ru(III) with optimum concentration range 1.3-11.3 ppm. The complex has absorption maximum at 515 nm with molar absorptivity 7.328×10^3 litre mole⁻¹ cm⁻¹.

THE reaction between promazine hydrochloride (PMH) and ruthenium(III) does not appear to have been studied so far. We have studied this reaction and proposed PMH as a sensitive reagent for the spectrophotometric determination of Ru(III). The proposed method offers the advantages of simplicity, sensitivity and stability without the need for extraction.

Ruthenium(III) chloride (M/s Johnson Matthey; 0.989 g) was dissolved in dilute hydrochloric acid (AR) and diluted to 1 litre to give 1M with respect to the acid. It was standardized gravimetrically by the thionalide method. The stock solution was further diluted to give a standard solution containing 20 µg Ru(III)/ml. A known amount of PMH (John Wyeth) was dissolved in doubly distilled water, solution standardized by the Ce(IV) sulphate method¹ and stored in an amber bottle in a refri-

gerator. Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

Procedure — Sample solution containing 5 to 298.5 µg of Ru(III) was transferred to a 25 ml volumetric flask and to this was added 7.5 ml of 5M sulphuric acid (AR) and 4.5 ml of 0.2% PMH solution. The solution was diluted up to the mark with doubly distilled water, mixed thoroughly and the absorbance measured at 515 nm after 10 min against a reagent blank prepared in the same way. Ruthenium concentration of the sample solution was calculated by means of a calibration curve.

PMH forms a red-coloured complex with Ru(III) at room temperature in the presence of sulphuric, hydrochloric or phosphoric acid. The sensitivity of the reaction and stability of the red colour depend on the nature and strength of the acid medium. The sensitivity in three acid media is in the order of $H_2SO_4 \approx HCl > H_3PO_4$. The maximum colour development takes place after 10 min in 1.25-2.0M sulphuric or 2.0-2.70M phosphoric acid and after 50 min in 1.5-3.0M hydrochloric acid. The colour of the red complex in H_2SO_4 , HCl and H_3PO_4 is stable for 12, 3 and 12 hours respectively. Though the stability of Ru-PMH complex in H_3PO_4 is 12 hr, the sensitivity (0.0217 µg/cm²) is very much less and hence the sulphuric acid medium has been selected.

Maximum absorbance is achieved in 1.25-2.0M sulphuric acid solution. The complex formation is incomplete at acidities lower than 1.25M H_2SO_4 . The reagent undergoes slow oxidation at acidities higher than 2.0M H_2SO_4 . The complex exhibits maximum absorbance at 510-520 nm; the reagent does not absorb around this wavelength.

It is found that a twenty-nine-fold molar excess of the reagent is necessary in order to ensure complete complexation. The absorbance values remain constant in the temperature range of 5-70°C. The order of addition of reagents is not critical. Beer's law is valid over the ruthenium concentration 0.2-11.94 ppm. The optimum concentration range evaluated by Ringbom's method² is 1.3-11.3 ppm. The molar absorptivity and sensitivity index are 7.328×10^3 litre mole⁻¹ cm⁻¹ and 0.0138 µg/cm² respectively.

The sensitivity of the proposed method is more than that of prochlorperazine maleate³, thioridazine hydrochloride⁴ and dithioamide⁵ which have been proposed as spectrophotometric reagents for ruthenium. The sensitivity of the present method is less than that of 4-hydroxy-3-nitroso-5,6-benzocoumarin⁶, 2,3-diaminopyridine⁷ and thioviolic acid⁸ which are used for the determination of ruthenium in the same range.

The red Ru-PMH complex is cationic in nature since the red colour is retained on the cation exchange resin.

The following amounts (µg/ml) of foreign ions are found to give an error of $\pm 1.5\%$ in the determination of 4 µg of Ru(III) per ml: Palladium(II) 0.3, Os(VIII) 0.8, Rh(III) 12, Ir(III) 12, Pt(IV) 4.0, Au(III) 0.2, Co(II) 480, Cu(II) 480, Ni(II) 400, U(VI) 615.8, Fe(III) 1.5, Zr(IV) 1214, Mo(VI) 200, Ce(IV) 0.2, chloride 4004.7, bromide 9365, iodide 1.5,