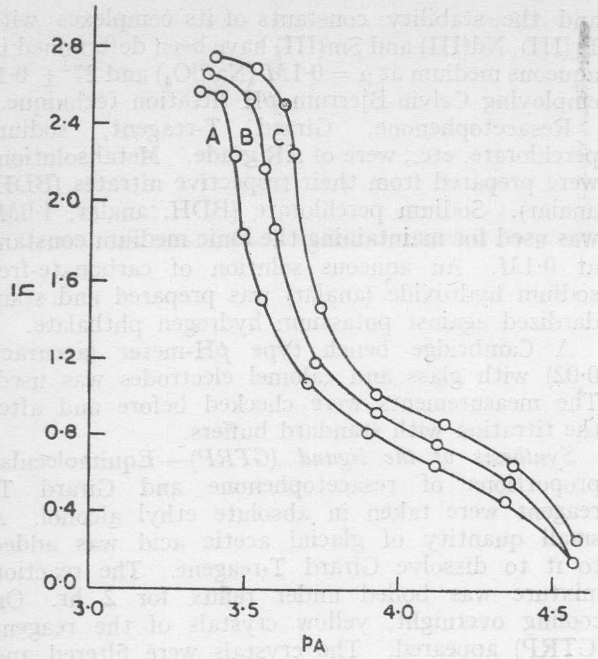

Fig. 1 — Formation curves of metal-GTRP systems [Curve A, Pr(III)-GTRP system; curve B, Nd(III)-GTRP system; and curve C, Sm(III)-GTRP system]

TABLE 1 — VALUES OF STEPWISE STABILITY CONSTANTS OF METAL CHELATES

	log K_1	log K_2	log K_3	log β_3	$-\Delta F$ (kcal)
			Pr(III)		
(a)	4·33	3·55	3·43	11·31	15·53
(b)	4·31	3·51	3·45	11·27	
	4·32	3·53	3·44	11·29	
	(±0·01)	(±0·02)	(±0·01)	(±0·02)	
			Nd(III)		
(a)	4·41	3·65	3·54	11·60	15·94
(b)	4·38	3·63	3·52	11·53	
	4·40	3·64	3·53	11·57	
	(±0·01)	(±0·01)	(±0·01)	(±0·03)	
			Sm(III)		
(a)	4·45	3·74	3·63	11·82	16·24
(b)	4·46	3·72	3·61	11·79	
	4·46	3·73	3·62	11·81	
		(±0·01)	(±0·01)	(±0·01)	

(a) Extension of Bjerrum's method.
(b) Graphical method.

Sm(III) forms stronger complexes than Nd(III) and Pr(III). This has been confirmed by the formation curves (Fig. 1). The $\bar{n}$ values go beyond 2·50 thereby indicating metal: ligand ratio 1:3. The chelate stability constants have been calculated at *p*H <6·0 as the complexation was complete by that *p*H (Table 1). The formation constants increase regularly with decrease in ionic radius. This is in accordance with lanthanide contraction order. In general log K_1>log K_2>log K_3 for a given metal. The values of overall change in free energies ($\Delta F = -RT \ln K$) are also calculated at 27° ± 0·1°.

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Biamperometric Determination of Au(III) & of Au(III) & U(VI) in Their Binary Mixtures

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The differences in formal redox potentials of the couples Au^{3+}/Au^0 and U^{6+}/U^{4+} enable the reducing agent sodium dithionite to react with Au(III) first, leaving U(VI) unaffected. After the completion of the reaction with Au(III), U(VI) is titrated with dithionite. The results obtained are good and the reaction is stoichiometric. The method is quick, simple, sensitive and precise.

VARIOUS methods[1-6] are available for the quantitative determination of Au(III). Sodium dithionite is a strong reducing agent and has been used for the estimation of various metal ions[7]. Uranium(VI) has been estimated amperometrically using sodium dithionite[8] as a reductant at an applied potential of 250 mV. In this note a simple biamperometric method is described for determining Au(III) in its pure salts and also for determining Au(III) and U(VI) in their binary mixture employing sodium dithionite as a reductant.

Sodium dithionite solution was prepared and standardized against ceric sulphate as described previously[7]. Au(III) chloride solutions were prepared and standardized as usual. Amperometric titrations were carried out using a modified circuit similar to those used by Foulk and Bawden[9] and Stone and Scholten[10]. Equivalence points were obtained graphically.

Determination of Au(III) — The normal redox potential of the system Au^{3+}/Au^0 ($E_0 = 1{\cdot}42$ V) depends only to a very small extent on acidity of the medium, therefore, for the quantitative determination of Au(III) by dithionite the medium was 0·1*N* sulphuric acid. Sodium dithionite reacted with Au(III) which formed a reversible couple with Au(0). The limiting current for the Au(III)/Au(I) system first increased, reached a maximum and then decreased to a minimum constant value corresponding to the complete reduction of Au(III) to Au(0). End points were reproducible and the results were quantitative.

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Determination of Au(III) and U(VI) in their binary mixtures — The determination of Au(III) and U(VI) depended on the differences in their formal redox potentials. Couples involved in the titration were titrated stepwise. Gold was determined in 0·1*N* sulphuric acid medium at an applied potential of 200 mV. Under these conditions U(VI) did not interfere in the determination of Au(III). After the completion of reaction with Au(III), as indicated by a drop in galvanometer deflection to a constant value, dithionite began to react with U(VI) at the same applied potential. The limiting current began to decrease and reached a minimum after the complete reduction of U(VI). The titration was continued till the galvanometer deflection corresponding to the reduction of U(VI) to U(IV) attained a constant value.

The results are reproducible and accurate. The method is quick and simple.

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Further Studies on Spectrophotometric Determination of Mg(II) with Eriochrome Black T

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The colour intensity of the Mg-Eriochrome Black T complex in buffered solutions containing amines is found to depend upon the *p*H, nature and concentration of the buffer used. The 1 : 2 complex of Mg-Erio T forms mixed complexes with different amines used for buffering, influencing the sensitivity of the method. Di- and tri-ethanolamines, hydrazine and hexamine enhance the sensitivity while ammonia, hydroxylamine and monoethanolamine decrease it.

The most suitable spectrophotometric method[1] for the determination of Mg^{2+} is based upon measurement of the intensity of the purple-red colour developed when Mg^{2+} ions are allowed to react with Eriochrome Black T (Erio T) in basic medium. In the present work, the dependence of the intensity of Mg-Erio T colour on the nature of the buffer medium and *p*H of solution as well as the stoichiometry of Mg-Erio T complex are investigated. Seven different media containing different amine derivatives and 0·1% ammonium chloride for buffering have been tested.

Aliquots of the standard magnesium solution were diluted in a 10 ml measuring flask with the buffer solution containing a definite concentration (0·008%) of Erio T, adjusting the *p*H to the desired level. The concentration of Mg^{2+} in the final solution was 0·1-2·0 μg/ml. The absorbance of the wine-red colour was measured at 520 nm, the wavelength of maximum absorption.

It is observed that the colour intensity of Mg-Erio T complex is largely dependent upon the *p*H of the solution and the concentration of the amine in the medium. The absorbance increased with increasing concentrations of the buffer constituents in some media, e.g. in the presence of triethanolamine, diethanolamine, hydrazine hydrate and hexamine solutions. Reverse is true for buffers containing ammonia, hydroxylamine and monoethanolamine. The absorption spectra of the Mg^{2+}-Erio T complex in the presence and absence of amines, which bring about decrease in absorbance reveal that mixed complexes are formed. Also the decrease in absorbance can be explained in the light of the competition between the complexing properties of the constituents of the buffers and Erio T with magnesium ions. Negative deviation from Beer's law is observed at relatively high amine concentration; the concentration of Mg^{2+} beyond which the deviation occurs varies inversely with monoethanolamine concentration.

Eriochrome-T, being a polydentate reagent, forms five- or six-membered less strained rings[2] with Mg^{2+}. One can arrange the media studied according to decreasing order of absorbance as follows:

Triethanolamine > diethanolamine > hydrazine hydrate > ammonia > hexamine > monoethanol amine > hydroxylamine hydrochloride

which is the order of increased tendency of the amine to form complexes with metal ions.

The stoichiometry of the Mg-Erio T complexes was determined by the continuous variation[3], molar ratio[4] and slope ratio[5] methods, as well as by conductometric titrations. The results showed the formation of 1: 1, 1: 2 and 1: 3 (Mg-Erio T) complexes at different *p*H values. The 1: 1 complex formation is favoured at *p*H 8·5, 1: 2 at *p*H 10 and 1: 3 at *p*H 11.

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