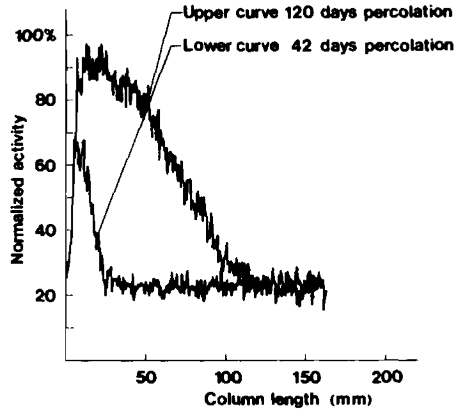

Fig. 2. Contamination profile of Am measured by γ-scanning during percolation step.

distribution observed in the fresh water leachate. The ultrafiltration experiments indicated that in the brine solution more than 50% of the radioactive colloids have dimension smaller than 0.1 μm. By comparison in the case of fresh water, 50% of the Am colloids were found to be smaller than 1 μm. The column contamination profile reported in Fig. 2 is therefore the result of two major mechanisms: colloidal filtration and the retention of soluble species. This second process however is hindered by the saturation of the active sites of the soil because of the extremely high ionic strength of the liquid phase.

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E13

Direct Spectrophotometric Determination of Cerium Sub-group Rare Earth Elements with m-Trifluoromethylchlorophosphonazo in the Presence of Yttrium Sub-group Elements in Nodular Cast Iron and Steel samples[+]

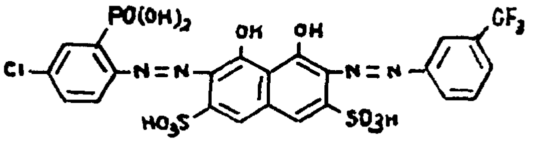
LI XINYI*, CHEN ZHENHUA, HE HUI and ZHANG HUASHAN

Department of Chemistry, Wuhan University, P.O. Box 430072, China

2,7-Bisazo derivatives of chromotropic acid have been used in the spectrophotometric determination of cerium sub-group rare earth elements, the most important being carboxynitrazo [1], due to their metallic complexes with high molar absorptivities. This reagent is applied to the analysis of ores with satisfactory results [2].

Recently, owing to the use of oxalic acid as masking reagent, selective spectrophotometric determination of cerium sub-group rare earth elements with CPAmN has been developed [3].

In the present work, the reaction of cerium sub-group rare earth elements with a new 2,7-bisazo derivative of chromotropic acid, the m-trifluoromethylchlorophosphonazo, is studied for its higher selectivity compared with the other reagents mentioned:



This paper describes the synthesis of the reagent and its use in the direct spectrophotometric determination of cerium sub-group rare earth elements in nodular cast iron and steel samples. The results obtained are favourable.

Reagents and Apparatus. Absorbance was measured on a Model UV-300 double-beam spectrophotometer and Model XG-125 spectrophotometer with 1-cm cells. The working standard solutions: 20 μg/ml.

Synthesis of m-Trifluoromethylchlorophosphonazo. 3-Trifluoromethylaniline was mixed with 20 ml of water and a solution of sodium nitrite (0.3 g in 8 ml of water), and then diazotized by adding 5 ml of 6 *M* hydrochloric acid by drops at 0–2 °C and stirring. The mixture is stirred 1 hr at 0–5 °C.

2 g Chlorophosphonazo I was dissolved in 30 ml of 5% lithium hydroxide solution and cooled to 0–2 °C. The diazotized solution prepared was added while stirring, the color of the solution changed from red to blue (the pH of the solution sometimes was adjusted to 9.5–10.5 with dilute lithium hydroxide solution or hydrochloric acid). After continuous stirring for 1 hr, the solution was allowed to stand overnight, acidified to pH 1–2 with hydrochloric acid, filtered and washed with 2 *M* hydrochloric acid 3 times.

The precipitate was dissolved in 80 ml of 5% lithium hydroxide solution and filtered. The solution was acidified to pH 1 with hydrochloric acid and then filtered and washed with 2 *M* hydrochloric acid 2–3 times. The product was dried at 50 °C, yielding 1.5 g of precipitate.

[+] Paper to be presented by Cheng Jai-kai, Laboratory of Analytical Chemistry, Dept. of Chemistry, Wuhan University, Wuhan, China.

Analysis of Nodular Cast Iron and Steel Samples. Weigh a 0.1000–4000 g sample into a 100 ml beaker and dissolve it in 20 ml of 6 N hydrochloric acid and 2 ml of 16 N nitric acid while heating. The solution was evaporated to 2–3 ml, cooled to the room temperature and 20 ml water was added filtering off any residue on fast filter paper and washing the residue and paper several times with dilute hydrochloric acid. Collecting the filtrate and washings in a 100 ml standard flask, diluted to the mark with water, mixed well.

An aliquot was tranferred containing not more than 20 μg of cerium sub-group rare earth elements into a 25 ml standard flask; 3 ml of 1 N hydrochloric acid, 5 ml of 10% oxalic acid and 2.5 ml of 0.05% m-trifluoromethylchlorophosphonazo solution were added and diluted to mark with water. The solution mixed well and absorbance measured at 677 nm in a 1 cm cell against nodular cast iron and steel for the absence of rare earths blank.

Absorption Characteristics. The absorption spectra of m-trifluoromethylchlorophosphonazo alone and of the complexes of cerium at 0.12 N hydrochloric acid have been studied. The spectra are shown in Fig. 1. The optimal wavelength for measurement of the cerium (or cerium sub-group elements, ΣCe) complex is found to be 677 nm.

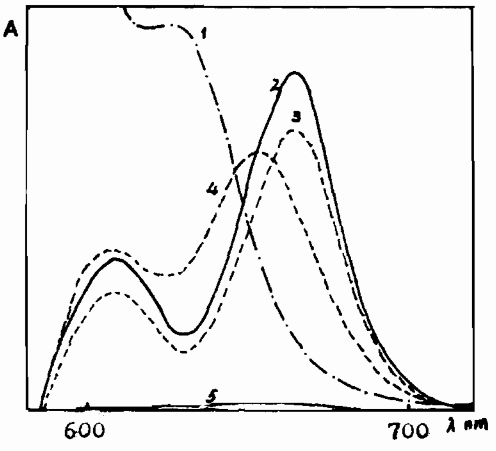


Fig. 1. Absorption spectrum. 1. Reagent against water. 2. Ce-reagent. 3. Ce-reagent, in the presence of 5 ml of 10% oxalic acid against reagent blank. 4. Yb-reagent. 5. Yb-reagent, in the presence of 5 ml of 10% oxalic acid against reagent blank. Ce 10.0 μg; Yb 10.0 μg.

A greater amount of oxalic acid slightly depresses the absorption of the cerium complex. In the same condition, ytterbium is almost completely masked.

Effect of pH. We have been studying the effect of HCl, HNO_3 and H_3PO_4 on the colour reaction. For the determination of cerium (or ΣCe) in the presence of yttrium sub-group elements (ΣY), the addition of 2–4 ml of 12 N hydrochloric acid was optimal. Hence a 3 ml addition of 12 N hydrochloric acid was chosen for the determination of cerium, which corresponded to 0.12 N hydrochloric acid in the final solution.

Effect of Time. The coloured complexes were formed instantly at room temperature. Their absorbances were stable for at least 6 hr.

Effect of Reagent Concentration. The chosen final concentrations of the reagent (2–3 ml of 0.05% m-trifluoromethylchlorophosphonazo, 5 ml of 10% oxalic acid) are those giving maximum absorbance.

Amounts of 5 ml of 10% oxalic acid solution were added for masking of iron and yttrium sub-group elements. A greater amount of oxalic acid would weaken the absorbance of the cerium complex. Therefore, an addition of 5 ml of 10% oxalic acid is recommended.

Beer's Law. In the absence of oxalic acid Beer's Law was obeyed for 0–25 μg/25 ml of cerium. In the presence of 20 mg iron and 5 ml of 10% oxalic acid Beer's Law was obeyed for 0–20 μg/25 ml of cerium or cerium sub-group elements.

The apparent molar absorptivities of lanthanum, cerium, praseodynium and neodymium at 677 nm were 9.2×10^4, 9.3×10^4, 9.8×10^4 and 9.0×10^4 l^{-1} mol^{-1} cm^{-1}, respectively.

Effect of Foreign Ions. An error of 10% in amount is considered tolerable for the determination of 10.0 μg of cerium. The following ions when present up to the amount (in mg) shown in brackets, do not interfere in the determination of 10 μg of cerium: Fe(III) 20, Al(III) 20, Ca(II) 0.24, Mg(II) 15, Ni(II) 2, Mn(II) 12, Ba(II) 0.23, Cu(II) 1.8, Co(II) 5.3, Pb(II) 3, Cd(II) 25, Zn(II) 12, Bi(III) 2, Cr(III) 6, Mo(VI) 25, W(VI) 22, Zr(IV) 2, Ti(IV) 0.35, V(V) 2, Si(IV) 22, NH_4^+ 22, $SO_4^=$ 22, Th(VI) 0.002. As shown, most of the ions did not interfere with the determination, 20 mg iron(III) and 20 mg of Al(III) were tolerable.

Comparison with Other Reagents. Some results obtained in the study of reagent m-trifluoromethylchlorophosphonazo for the determination of cerium are compared with those obtained with CPAmN. Absorption spectra for both cerium complexes are similar. The optimum pH is different. m-Trifluoromethylchlorophosphonazo may react in 0.12 N hydrochloric acid, the change of absorbance with acid is very small. Due to the higher selectivity of m-trifluoromethylchlorophosphonazo, greater interference is found by using CPAmN as reagent in the determination.

Analysis of Some Synthetic Samples. Table I gives results for some synthetic samples, showing that the method is satisfactory.

TABLE I. Recovery of Cerium Added to Selected Synthetic Samples.

Added (ΣY)	Ce, μg		Recovery (%)
	Added	Found	
2	7	6.9	98.6
5	10	10.3	103.0
5	12	12.2	101.0
7	15	14.6	97.3
10	10	11.0	110.0

Applications. The proposed method has been applied to the determination of cerium sub-group elements in nodular cast iron and low alloy steel (Table II).

TABLE II. Determination of Cerium Sub-group Elements in Iron and Steel.

Sample	Composition %	Found %	
Low alloy steel			
1	0.052	0.0508	0.051
2	0.029	0.0293	0.0297
3	0.031	0.0313	0.031
4	0.0205	0.0203	0.0203
5	0.0354	0.0346	0.0342
6	0.082	0.0814	0.0814
Nodular cast iron			
1	0.022	0.0236	0.0236
2	0.046	0.0468	0.0468
3	0.085	0.082	0.082

Table II gives results for some typical samples showing the method is considered satisfactory.

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E14

A New Fluorimetric Technique for Low Levels Uranium Determination using Lifetime Measurements

P. MAUCHIEN

Commissariat à l'Energie Atomique, DCAEA/SEACC, B. P. 6, F92260 Fontenay-aux-Roses, France

A current method used for the determination of trace uranium is the fluorimetric technique. Many scientists studied the emission mechanism and it has been showed that phosphoric complexes give the best fluorescence efficiency.

In 1976 a commercially available laser was introduced by Scintrex Ltd for the direct determination of trace amounts of uranium in water. This new instrument is based on laser induced fluorescence. Its use was described in details by Robbins [1] and a critical study of the performances was made by Campen and Bächmann [2]. The excitation source is a nitrogen laser emitting ultraviolet radiation of 3371 Å. As any fluorescence from organic matter in the water is superimposed on the uranyl phosphate complex fluorescence, a discrimination by time is provided. After each pulse an electronic gating system is employed to separate the very long uranyl fluorescence from the very intense but very short organic matter fluorescence.

This technique is suitable for detection of uranium at very low levels (about 0.05 μg l^{-1}), however the apparatus has some drawbacks:

– Uranium fluorescence spectrum which is characteristic, cannot be obtained.

– Lifetime acquisition allowing to stress the presence of quenching species in solution is not possible. Due to the very long lifetime of uranyl in the excited state (100 to 200 μs in 0.75 *M* phosphoric acid medium), a lot of constituents can participate to quench fluorescence.

As a result this procedure for the determination of trace implies to use the internal standard method, which is time consuming and increases analytical waste. This last point can be a severe drawback to this technique for the determination of trace uranium in radioactive waste [3].

We developped in our laboratory a new technique, by-passing the previous problem of the internal standard method for the determination of trace uranium. The idea is that the laser pulse duration being very short compared to the fluorescent lifetime in the excited state, population of the excited molecules will not reach the steady state before the end of irradiation.

With some assumptions, concentration in excited molecules at the end of irradiation time ($|UO_2{}^{2+}|^*_{t.irr}$) leads to eqn. (1):

$$|UO_2{}^{2+}|^*_{t.irr} = \epsilon I_1 |UO_2{}^{2+}| x t.irr \qquad (1)$$

ϵ = molar absorption coefficient in e-basis. I_1 = intensity of the excitation radiation. $|UO_2{}^{2+}|$ = unknown concentration. t.irr = duration of laser pulse.

Fluorescence being proportional to concentration in excited molecules, it leads to eqn. (2):

$$F_{t.irr} = \frac{1}{\tau_o} k \epsilon I_1 t.irr |UO_2{}^{2+}| \qquad (2)$$

k = apparatus factor. τ_o = natural lifetime of the excited state. $F_{t.irr}$ = fluorescence just after laser pulse.