

Sensitive and Selective Fluorimetric Determination of Scandium With Salicylaldehyde Carbohydrazone

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The optimum conditions for scandium complex formation with salicylaldehyde carbohydrazone are described. A simple, rapid, sensitive and selective method for the fluorimetric determination of scandium has been developed. The reaction is carried out at pH 2.7–5.2 in aqueous ethanol (60% v/v ethanol). A limit of detection for scandium of 0.2 ng ml^{-1} is obtained with a relative standard deviation of $\pm 1.5\%$. The effect of interferences was also studied. Synthetic solutions containing known amounts of the rare earth elements, in addition to scandium, yttrium, thorium, and iron in proportions typical of some international standard reference rocks are prepared and scandium is determined using the proposed method.

Keywords: Scandium determination; fluorimetry; salicylaldehyde carbohydrazone; rock analysis

Scandium is found naturally with yttrium and the lanthanides in a variety of rocks and minerals. Therefore, in order to obtain accurate values for trace amounts of scandium in rocks and other complex materials, it is necessary, before the final determination by spectrophotometry or fluorimetry, to separate it completely from other elements such as yttrium and the lanthanides, because of the similarity in chemical and physical properties of these elements. Several separation procedures, e.g., fractional crystallization,¹ liquid–liquid extraction² and ion-exchange,³ have been used for this purpose.

In recent literature, various methods for the determination of scandium have been proposed, several of which are spectrophotometric^{4–11} or fluorimetric^{12–19} and involve the use of organic reagents.

In this paper, the use of salicylaldehyde carbohydrazone (SACH) as a new ligand for the fluorimetric determination of Sc^{III} is described. Detailed studies on the complexation equilibria of SACH with Sc^{III} in 60% ethanol have been carried out. Various aspects of the chemistry of the reaction are investigated, and a procedure for the determination of scandium is proposed. This method can be used to determine 0.7 ng ml^{-1} of scandium, thus it is more sensitive than most previous methods.

Experimental

Reagents

All chemicals were of analytical-reagent grade. Glass-distilled and de-ionized water was used throughout.

Salicylaldehyde carbohydrazone was synthesized by the following procedure; 0.9 g of carbohydrazide (Aldrich) was dissolved in 10 ml of distilled water, and 3.1 g of salicylaldehyde (Aldrich) dissolved in 10 ml of ethanol were added. The mixture was refluxed and the product filtered, then crystallized from ethanol and dried in a vacuum desiccator (yield 60%). The product had a melting-point of $235 \pm 1^\circ\text{C}$ and elemental analysis gave the following results: C, 59.90%; H, 5.12%; N, 18.23%; and $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_3$ has the composition C, 60.00%; H, 4.69%; and N, 18.79%. Solutions of $1 \times 10^{-3} \text{ mol dm}^{-3}$ of SACH in ethanol were prepared daily.

Stock standard Sc^{III} solution (0.629 g l^{-1}) was prepared by dissolving the oxide in 7 mol dm^{-3} nitric acid. This solution was standardized by titration with ethylenediaminetetraacetic acid (Xylenol Orange indicator).

Buffer solution (pH 1.9) was prepared by mixing 250 ml of 0.2 mol dm^{-3} potassium chloride with 66 ml of 0.2 mol dm^{-3} hydrochloric acid and diluting to 1000 ml with de-mineralized water.

Apparatus

A Perkin-Elmer fluorescence spectrophotometer, Model MPF-43A, was used for recording fluorescence spectra and a Perkin-Elmer fluorescence spectrophotometer, Model LS-5 was used for measurements at fixed wavelengths, both instruments were equipped with 1 cm quartz cells.

A Crison Digit-501 pH meter was used for all pH measurements (throughout this paper pH is used to denote the pH meter reading and not the actual concentration of hydrogen ions in solution).

Procedure

Into a 25 ml calibrated flask, transfer 5 ml of buffer solution and an aliquot of the sample solution (less than 5 ml) containing $0.0175\text{--}25 \mu\text{g}$ of scandium. Add 12 ml of ethanol (to prevent precipitation of the reagent), 3 ml of $1 \times 10^{-3} \text{ mol dm}^{-3}$ SACH solution in ethanol and dilute to volume with distilled water. Measure the fluorescence at 452 nm, using excitation at 375 nm at 25°C . Determine the amount of scandium in the sample from a calibration graph prepared under the same conditions. Alternatively, use a standard additions procedure when interfering ions are present and for samples with a high salt content.

Synthetic Solutions

Synthetic solutions containing Sc, Y, Th, the lanthanides and iron in proportions typical of some international standard reference rocks, GA, NIM-G and NIM-18/69,²⁰ were prepared and scandium was determined by the recommended procedure. For this purpose stock solutions of the individual elements were prepared by dissolving 100.0 mg of the pure oxide of each element in hot dilute nitric acid, cooling to room temperature and diluting to 100 ml in a calibrated flask (final acidity $1 \text{ mol dm}^{-3} \text{ HNO}_3$). For cerium the stock solution was obtained by dissolving cerium dioxide in a hot solution of nitric acid and hydrogen peroxide. Solutions were stored in stoppered polyethylene bottles. Solutions of lower concentrations ($0.1\text{--}100 \text{ mg ml}^{-1}$) were obtained by dilution with $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$. Synthetic mixtures were prepared by mixing different volumes of these individual solutions.

Results and Discussion

Reagent Properties

The solubilities in several solvents were determined by the Wittenberger²¹ method at 25°C . The reagent is soluble in dimethylformamide, methanol, ethanol, isobutyl methyl

ketone (IBMK), and slightly soluble in water, chloroform, hexane and benzene. Solutions of the reagent (1×10^{-3} mol dm $^{-3}$) in ethanol, dimethylformamide, ethanol–water and dimethylformamide–water mixtures at different pH values were stable for more than a day.

The dissociation constants were determined using spectrophotometry from the variation of absorbance with the pH. The reagent shows two ionization steps. As the molecule is symmetrical and the distance between the dissociable protons is relatively large, the values of the ionization constants for corresponding groups in the two halves would be expected to be similar and thus be indistinguishable by spectrometry. The pK value of the first ionization step was calculated from the variation of absorbance with pH, at different wavelengths, by the Goldsmith and Stenström²² and Sommer²³ methods; the mean value found was 10.5. For the calculation of the second pK value, in a highly basic medium, the acidity function²⁴ H^+ was used: $pK = H^+ + \log[HL]/[L^+]$; when $[HL] = [L^+]$, $H^+ = pK$.

Values of H^+ have been tabulated by Schwarzenbach and Sulzberger²⁵ for known concentrations of sodium hydroxide. The absorbances at different wavelengths were plotted against H^+ , and the inflection point calculated. The value obtained was 13.6.

The reaction of the reagent with 40 metal ions at various pH values in a medium containing 52% v/v ethanol, in order to avoid the precipitation of reagent, were investigated. The reagent acts as a non-selective chelating agent towards many metal ions. Coloured reaction products are formed with Cu^I, Cu^{II}, Fe^{III}, V^V, Ni^{II}, Co^{II} and Pd^{II}, and fluorescent complexes with aluminium, gallium, scandium, zinc, yttrium and thorium. The scandium complex shows an intense fluorescence, which can be used for its determination.

Emission Spectra

In order to determine the optimum working wavelength, the spectral characteristics of the Sc^{III}–SACH complex were studied at various pH values. Fig. 1 shows the spectra obtained in acidic, neutral and basic media. From these spectra it can be seen that maximum emission was obtained at 452 nm with excitation at 375 nm in an acidic medium. The pH was adjusted to 3, 6 and 12 by adding dilute potassium hydroxide (0.01 mol dm $^{-3}$) or hydrochloric acid (0.01 mol dm $^{-3}$) solutions.

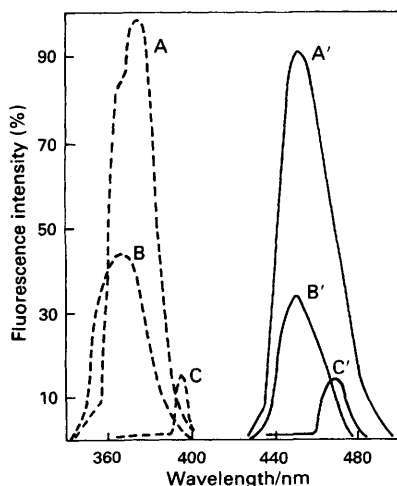


Fig. 1 Fluorescence excitation (broken line) and emission spectra (solid line) of the Sc^{III}–SACH complex: A, A' at pH 3; B, B' at pH 6; and C, C' at pH 12

Effect of pH

The pH of the medium had a major effect on the fluorescence intensity, Fig. 2 shows the dependence of fluorescence on the pH of the scandium chelate at selected wavelengths. This figure clearly illustrates that the optimum pH range for complex formation is 2.7–5.2. The fluorescence decreases drastically at both lower and higher pH values. All subsequent studies were carried out at pH 2.8–2.9 (under these conditions, emission from the reagent blank at 452 nm was negligible). A buffer of potassium chloride–hydrochloric acid, pH 1.9, was selected because the volume of ethanol added in the preparation of the solutions increased the pH by more than 1 unit. The volume of the added buffer (3–7 ml) had no effect.

Influence of Ethanol Content in the Medium

As the SACH was dissolved in ethanol, the effect of this solvent on the system was studied. The results obtained are shown in Fig. 3. It can be seen that the fluorescence intensity of the complex increases when the ethanol content in the medium increases, hence a medium containing 60% ethanol was selected. In this medium, the fluorescence intensity remains constant for at least 60 min.

Influence of Temperature and Order of Addition of Reagents

The normal fluctuation in laboratory temperature had a negligible effect on scandium recovery. All fluorescence measurements were carried out at room temperature.

The order of addition of the reagents was investigated and found to have an effect on the fluorescence. Therefore, the following sequence was selected as the optimum: buffer, sample, solvent and the ligand. Under these conditions, chelate formation is instantaneous. When any other order of addition was used, maximum fluorescence was obtained only slowly, hence solutions could not be measured immediately.

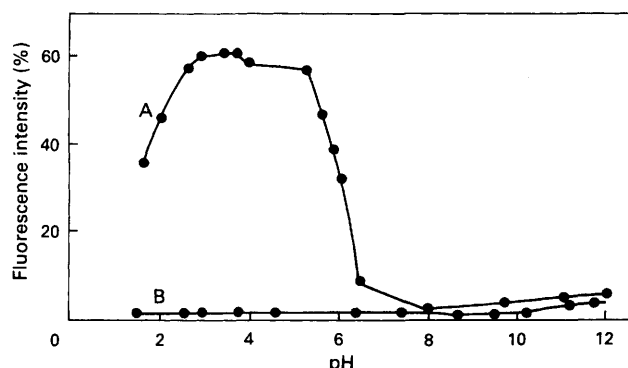


Fig. 2 Influence of pH on the fluorescence of A, the Sc^{III}–SACH complex and B, the reagent alone, under the same conditions

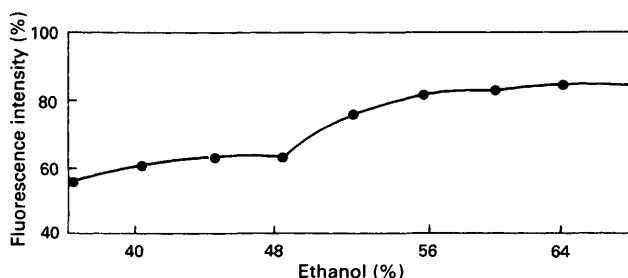


Fig. 3 Influence of percentage of ethanol on the fluorescence of the Sc^{III}–SACH complex

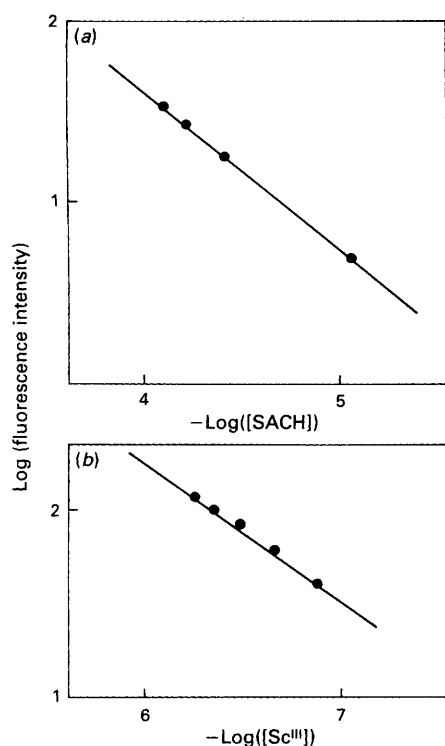


Fig. 4 Stoichiometry of the Sc^{III}-SACH complex

Influence of Reagent Concentration

The influence of the reagent concentration on the fluorescence intensity obtained from solutions containing 20 ng ml⁻¹ of Sc^{III} was studied under the fixed conditions of the recommended procedure. The fluorescence intensity increases with the reagent concentration up to 8×10^{-5} mol dm⁻³ then remains constant between 8×10^{-5} and 2×10^{-4} mol dm⁻³. For reagent concentrations higher than 2.4×10^{-4} mol dm⁻³ the intensity decreases, owing to fluorescence inversion phenomena. A reagent concentration of 1.2×10^{-4} mol dm⁻³ was chosen as optimum in order to ensure a sufficient excess of reagent.

Composition of the Complex

The Bent and French method,²⁶ in the presence of 5 ml of pH 1.9 potassium chloride-hydrochloric acid buffer (Fig. 4), was used to determine the ratio of SACH to scandium in the complex. The results obtained indicated, within the limits of experimental error, that the composition of the complex is 1 : 3 (ion : ligand).

Analytical Characteristics

There was a linear relationship between the scandium concentration and the fluorescence intensity over the range 0.7–1000 ng ml⁻¹ of scandium. A negative deviation from linearity was observed at higher scandium concentrations.

The precision of the method was studied by the analysis solutions containing known amounts of scandium. The results from the determination of 10 ng ml⁻¹ of scandium showed a maximum relative error of $\pm 1.5\%$. The limits of detection and determination of the method were established according to American Chemical Society Committee on Environmental Improvement definitions,²⁷ and the values found were 0.2 and 0.7 ng ml⁻¹, respectively.

Table 1 Effect of foreign ions on the determination of 10 ng ml⁻¹ of scandium

Amount tolerated without masking agent/ng ml ⁻¹	Foreign ions
>20 000	Ba ^{II} , Ca ^{II} , Mg ^{II} , Pb ^{II} , Se ^{IV} , Hg ^{II} , Mn ^{II} , Tl ^I , In ^{III} , Zr ^{IV} , W ^{VI} , Cr ^{III} , Co ^{II} , Sr ^{II} , Sb ^{III} , La ^{III} , Ce ^{III} , Tm ^{III} , Er ^{III} , Ho ^{III} , Pr ^{III} , Eu ^{III} , Nd ^{III} , Dy ^{III} , Tb ^{III} , Sm ^{III} , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , I ⁻ , NO ₂ ⁻ , IO ₄ ⁻ , SeO ₃ ²⁻ , WO ₄ ²⁻ , dimethylglyoxime, ascorbic acid
15 000	Cd ^{II} , UO ₂ ^{II} , ClO ₃ ⁻ , AsO ₄ ³⁻ , AsO ₂ ⁻ , IO ₃ ⁻ , S ₂ O ₃ ²⁻ , citrate, borate, EDTA, Y ^{III} , C ₂ O ₄ ²⁻
5 000	Tartrate
500	Fe ^{III} , VO ₃ ⁻ , Cu ^{II}
10	Ga ^{III}

Table 2 Interferences in the presence of masking agents (concentration of Sc^{III}, 10 ng ml⁻¹)

Foreign ion	Amount tolerated with masking agent/ng ml ⁻¹	Masking agent/ng ml ⁻¹
Bi ^{III}	15 000	I ⁻ , 20 000
Ni ^{II}	10 000	Dimethylglyoxime, 20 000
Al ^{III}	10 000	PO ₄ ³⁻ *, 40 000
Zn ^{II}	10 000	Citrate, 10 000
Th ^{IV}	10 000	Citrate, 10 000
Cu ^{II}	5 000	S ₂ O ₃ ²⁻ , 15 000
VO ₃ ⁻	2 500	Ascorbic, 20 000
Fe ^{III}	2 500	Ascorbic, 20 000

* No interferences at the indicated level

Table 3 Determination of trace amounts of scandium in synthetic samples

Sample	Sc ^{III} added/ μ g ml ⁻¹	Sc ^{III} found/ μ g ml ⁻¹
GA	0.050	0.050 \pm 0.002
	0.250	0.240 \pm 0.008
	0.500	0.490 \pm 0.002
NIM-G	0.050	0.060 \pm 0.003
	0.250	0.250 \pm 0.005
	0.500	0.500 \pm 0.002
NIM-18/69	0.050	0.060 \pm 0.003
	0.250	0.240 \pm 0.004
	0.500	0.510 \pm 0.002

* Mean of four determinations

Effect of Foreign Ions

In order to assess the possible analytical applications of this fluorescence reaction, the effect of some foreign ions was determined by carrying out determinations of 10 ng ml⁻¹ of scandium in the presence of each of these ions (Table 1). An interferent to scandium ratio of 2000 m/m was tested, and if interference occurred, the ratio was progressively reduced until interference ceased. The criterion for an interference was a fluorescence intensity value varying by more than 5% from the expected value for scandium alone. The tolerance level for some metal ions can be increased by the addition of masking agents (see Table 2).

Applications

The recommended procedure for the determination of Sc^{III} was applied with some synthetic samples for validation (Table 3). Therefore, synthetic solutions containing yttrium, cerium, scandium, thorium, and the lanthanides and iron in proportions typical of some standard reference rocks were

Table 4 Characteristics of reagents for the fluorimetric determination of scandium

Reagent	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	Sensitivity/ ng ml^{-1}	Applicable range/ $\mu\text{g ml}^{-1}$	Remarks	Applicable for	Reference
Salicylic acid and Rhodamine S	552	580			Mixed-ligand complex	Mineral samples	12
2-Phenylquinoline-4-carboxylic acid and Rhodamine S	556	580		0.007–0.02	Mixed-ligand complex	Mineral samples	12
1-10-Phenanthroline and Eosine B	540	570		0.05–1	Extraction with benzene	Rocks	13
5-Hydroxyflavone and its derivatives	365	430		0.0–0.6	Extraction with benzene		14
N-(2-hydroxy-1-naphthyl)aniso-hydrazide	—	505	60	0.5–25	Aqueous Me_2CO medium	Titanium products	15
Rhodamine B			2		Extraction with benzene		16
5,7-Dinitro-8-hydroxyquinoline and unsubstituted Rhodamine	420	520		0.002–2	Extraction with benzene		17
Kaempferol(3,5,7-trihydroxy-2-[4- hydroxyphenyl]-4H-1-benzopyran- 4-one)	436	510	8	0.014–0.04	40% Me_2CO	Carbonate rocks and natural water	18
2-Hydroxy-1-naphthaldehyde semicarbazone	405	445			Extraction with acetone + benzene	Minerals	19
SACH	375	452	0.2	0.0007–1.0	60% ethanol	Minerals	This work

prepared as described under Experimental. The composition of these samples (in $\mu\text{g ml}^{-1}$) was as follows. GA: Y, 1.70; Pr, 0.70; Nd, 2.00; Sm, 0.52; Eu, 0.08; Tb, 0.05; Dy, 0.27; Ho, 0.05; Er, 0.15; Tm, 0.02; Fe, 10; Ce, 1.00; Th, 1.0. NIM-G: Y, 10.8; Pr, 2.0; Nd, 7.1; Sm, 1.8; Eu, 0.04; Tb, 0.3; Dy, 1.7; Ho, 0.5; Er, 1.35; Tm, 0.19; Fe, 10.0; Ce, 1.0; Th, 1.0. NIM-18/69: Ce, 6.4; Dy, 6.0; Er, 2.1; Eu, 4.3; Ho, 1.0; La, 3.6; Nd, 2.7; Pr, 43.0; Sm, 18.5; Tb, 2.6; Tm, 0.25; Y, 26.3; Fe, 10.0; Th, 1.0.

Conclusions

Several methods utilizing various organic reagents have been described in the literature for the fluorimetric determination of scandium. However, in general, these methods are tedious as they involve several extraction steps. For comparison purposes the characteristics of the Sc^{III} -SACH complex are given in Table 4 together with those of other Sc^{III} complexes used for fluorimetric determinations. Salicylaldehyde carbohydrazone offers a higher sensitivity and selectivity.

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References

- Sen Gupta, J. G., *Anal. Chim. Acta*, 1982, **138**, 295.
- Keil, R., *Fresenius Z. Anal. Chem.*, 1980, **303**, 188.
- Hugson, M. R., and Sen Gupta, J. G., *Am. Mineral.*, 1964, **49**, 937.
- Tikhonov, V. N., and Fedotova, S. N., *Zh. Anal. Khim.*, 1982, **37**, 1988.
- Onosova, S. P., and Kuncévitch, G. K., *Zh. Anal. Khim.*, 1965, **20**, 802.
- Tikhonov, V. N., Danilova, S. G., *Zh. Anal. Khim.*, 1980, **30**, 1264.
- Horiuchi, Y., and Nishida, H., *Bunseki Kagaku*, 1968, **17**, 756.
- Jurkevicitute, J., and Malat, M., *Collect. Czech. Chem. Commun.*, 1979, **44**, 3236.
- Tikhonov, V. N., and Pavlova, O. K., *Zh. Anal. Khim.*, 1982, **37**, 1809.
- Tikhonov, V. N., and Samarkina, V. T., *Khim. Khim. Tekhnol.*, 1978, **21**, 1116.
- Jarosz, M., and Marczenko, Z., *Anal. Chim. Acta*, 1984, **159**, 309.
- Kononenko, L. I., Bel'tyukova, S. V., and Poluektov, N. S., *Zh. Anal. Khim.*, 1975, **30**, 1716.
- Matveets, N. A., Akhmetova, S. D., and Scherbov, D. P., *Zh. Anal. Khim.*, 1977, **32**, 2146.
- Murata, A., Tominaga, M., Susuki, T., and Nakamura, M., *Bunseki Kagaku*, 1978, **227**, 788.
- Dolgorev, A. V., Sivak, N. S., Palnikova, T. I., and Gurevich, L. M., *Zh. Anal. Khim.*, 1979, **34**, 106.
- Kuz'yakova, N. Y., Deposited doc. 1983, VINITI 7085, Pt. 2, p. 184.
- Kuz'yakova, N. Y., Golovina, A. P., Chemleva, T. A., and Il'yakove, N. V., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1984, **25**, 58.
- Arkhipova, L. A., Zel'tser, L. E., Talipov, Sh. T., *Khim. Khim. Tekhnol.*, 1984, **27**, 1415.
- Deguchi, M., Shigamatsu, T., Morishige, K., Yamagachi, K., and Kumura, J. D., *Bunseki Kagaku*, 1986, **35**, 779.
- Sen Gupta, J. G., *Talanta*, 1985, **32**, 1.
- Wittenberger, W., *Chemische Laboratoriums Technik*, 4th edn., Springer-Verlag, Vienna, 1950, p. 101.
- Goldsmith, J., and Stenström, W., *Phys. Chem.*, 1926, **30**, 1683.
- Sommer, L., *Folia Fac. Sci. Nat. Uni. Purkynianae Brun.*, 1964, **5**, 1.
- Cookson, R. F., *Chem. Rev.*, 1974, **5**, 74.
- Schwarzenbach, G., and Sulzberger, P., *Helv. Chim. Acta*, 1944, **17**, 348.
- Bent, H. E., and French, C. L., *J. Am. Chem. Soc.*, 1941, **63**, 1568.
- ACS Committee on Environmental Improvement, *Anal. Chem.*, 1980, **52**, 2242.

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