Highly sensitive spectrofluorimetric determination of trace amounts of scandium with salicylaldehyde salicyloylhydrazone

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The fluorescent reaction of salicylaldehyde salicyloylhydrazone (SASH) with scandium was studied in detail. Based on this chelation reaction, a highly sensitive spectrofluorimetric method was developed for the determination of scandium in ethanol–water (1 + 1 v/v) medium at pH 5.0. Under these conditions, the Sc–SASH complex had excitation and emission maxima at 388 and 465 nm, respectively. The linear range of this method was 0.40–100 ppb and the detection limit was 0.12 ppb of scandium when a standard additions method was used in the assay. The molar ratio of scandium to the reagent was found to be 1 : 1. The effect of interferences was studied. The proposed method was successfully used to determine trace amounts of scandium in geological soil samples. Extraction with 1-phenyl-3-methyl-4-benzoylpyrazolone–benzene from formic acid–sodium formate medium (pH 3) was used to separate Sc from interfering elements in the soil samples.

Keywords: *Scandium determination; salicylaldehyde salicyloylhydrazone; spectrofluorimetry; soil analysis*

In recent years, aroylhydrazones, which contain the group –CONHN=CH–, have been tested as fluorescent reagents.[1,2] The formation of complexes with a coplanar structure is conducive to the production of fluorescence: the reaction of a metal ion with a chelating agent induces rigidity in the resulting molecule and tends to produce fluorescence.[3]

Scandium is found naturally with yttrium and the lanthanides in a variety of rocks and minerals. In order to obtain accurate values for trace levels of scandium in these samples, it is necessary to find a simple, rapid and sensitive method for determining this element.

In the recent literature, various methods for the determination of scandium have been proposed, several of which were spectrophotometric[1–7] or fluorimetric,[8–13] including the use of aroylhydrazones. Several separation procedures, such as fractional crystallization, liquid–liquid extraction and ion exchange, have been used to separate Sc from a large number of metal ions that form fluorescent and non-fluorescent complexes with organic reagents to quench the fluorescence of the scandium complex.

The characteristics of salicylaldehyde salicyloylhydrazone (SASH) and its application to the fluorimetric determination of aluminium have been reported.[14] In this work, the fluorescent reaction of SASH with scandium was studied. The fluorescence intensity of the complex was increased by the coplanar effect owing to the presence of aromatic rings at both ends of the reagent's molecule. The effects of various organic solvents and surfactants on the fluorescence of the complex were studied, and showed that maximum fluorescence could be obtained in the presence of a suitable amount of ethanol in the reaction system. Based on the complexation, a spectrofluorimetric method with high sensitivity was developed for the determination of scandium. The detection limit is 0.12 ppb of scandium, which is more sensitive than most previous methods[8–13] (see Table 3). The procedure is simple to perform and offers good precision and accuracy. Extraction with 1-phenyl-3-methyl-4-benzoylpyrazolone (PBMP)–benzene from an acidic medium (pH 3) was used to separate scandium from interfering elements in geological soil samples. The proposed method was applied to the determination of scandium in these samples with satisfactory results.

Experimental

Apparatus

All fluorescence measurements were carried out on a Perkin-Elmer (Norwalk, CT, USA) LS-5 spectrofluorimeter, equipped with a xenon lamp, 1.0 cm quartz cells and a Perkin-Elmer Model 561 recorder. All pH measurements were made with a pHS-3C digital pH meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass–calomel electrode.

Reagents

All chemicals used were of analytical-reagent or higher grade. De-ionized water was used throughout. A 1.00 mg ml^{-1} stock standard solution of scandium was prepared by dissolving 0.1530 g of the oxide in 100 ml of 6 mol l^{-1} hydrochloric acid. This solution was standardized by EDTA titration with Xylenol Orange as indicator. Working standard solutions were prepared by suitable dilution of this stock standard solution. A hydrochloric acid–ammonium acetate buffer (0.2 mol l^{-1}, pH 5.0) was used. SASH solution (1.0×10^{-3} mol l^{-1}) was prepared by dissolving 0.3340 g of the reagent (synthesized in-house[14]) in 1000 ml of absolute ethanol.

Spectrofluorimetric determination of scandium

In a 10 ml color comparison tube were placed 2.0 ml of buffer solution (pH 5.0), 0.5 ml of 1.0×10^{-3} mol l^{-1} SASH solution, 4.5 ml of absolute ethanol and an aliquot of the sample solution (< 3.0 ml) containing 0.004–1.0 μg of scandium. After dilution to volume with de-ionized water, the mixture was equilibrated at room temperature for 10 min, then the fluorescence intensity of the solution was measured was 465 nm with excitation at 388 nm against a reagent blank. A calibration graph was prepared under the same conditions. Interfering elements present in the sample could be removed by extraction with PMBP–benzene from an acidic medium (pH 3.0). A standard additions method was used to determine trace amounts of scandium in geological soil samples.

Results and discussion

Excitation and emission spectra

In order to determine the optimum working wavelength, the spectral characteristics of the Sc–SASH complex were studied

at various pH values. The corrected excitation and emission spectra (Fig. 1) showed that the wavelengths of maximum excitation and emission of the Sc–SASH complex in ethanol–water (1 + 1 v/v) medium at pH 5.0 were 388 and 465 nm, respectively.

Influence of experimental variables

The pH of the medium had an important effect on the fluorescence intensity of the Sc–SASH complex. The experimental result [Fig. 2(*a*)] showed that the optimum pH range for the complex formation was between 4.7 and 5.3. Therefore, a pH of 5.0 was fixed with the use of acetate buffer.

As the volume of the buffer added (from 1.0 to 3.0 ml) had little effect on the fluorescence intensity, 2.0 ml was used in subsequent experiments.

The chelation reaction was completed within 6–10 min at 20–40 °C. The fluorescence intensity reached a maximum 10 min after SASH had been added and remained constant for at least 2 h, after which it decreased slowly. The order of addition of the reagents was investigated and found to have an effect on the fluorescence. The sequence selected as the optimum was buffer, solvent, the ligand and sample. Hence, all the chelation reactions were carried out for 10 min at room temperature and all the subsequent fluorescence measurements were made at room temperature within 2 h with the same order of addition of the reagents.

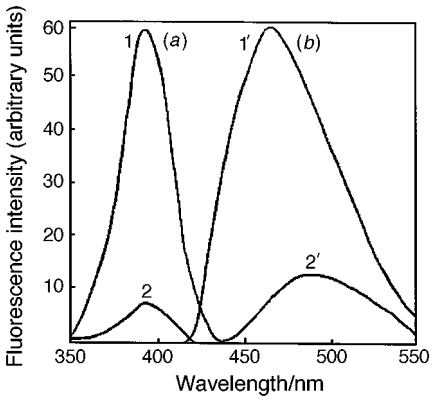

Fig. 1 (*a*) Excitation and (*b*) emission spectra of the Sc–SASH complex. The concentrations of Sc^{III} and SASH were 100 ppb and 5×10^{-5} mol l^{-1}, respectively, in ethanol–water (1 + 1 v/v) medium. Peaks: 1 and 1′, Sc–SASH complex; 2 and 2′, reagent blank.

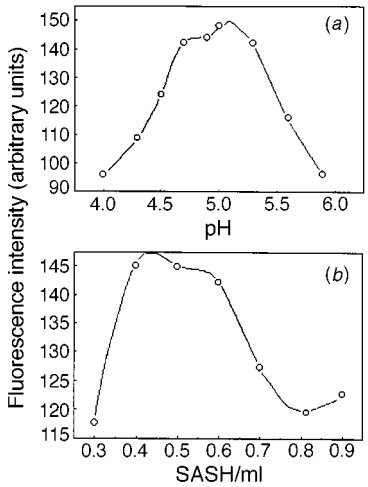

Fig. 2 Effect of experimental variables on the fluorescence of the Sc–SASH complex. The Sc^{III} concentration was 100 ppb in ethanol–water (1 + 1 v/v) medium. (*a*) Effect of pH; and (*b*) effect of amount of SASH.

The influence of the amount of SASH on the fluorescence intensity of a solution containing 100 ppb of scandium was studied under the conditions established above. The fluorescence intensity increased with increase in the amount of SASH up to 0.4 ml (1.0×10^{-3} mol l^{-1}), then remained constant between 0.4 and 0.6 ml and decreased slowly thereafter [Fig. 2(*b*)]. Therefore, 0.5 ml was selected to ensure a sufficient excess of the reagent throughout the experiments.

As SASH is slightly insoluble in water but soluble in ethanol, an ethanol–water medium was used. The effect of the ethanol content on the fluorescence intensity of the Sc–SASH complex was examined and the results are given in Table 1. It can be seen that the fluorescence intensity of the complex increased when the ethanol content in the medium increased, and the most suitable concentration range was 40–60% v/v. Therefore, a 1 + 1 v/v ethanol–water medium, containing 4.5 ml of absolute ethanol and 0.5 ml of 1.0×10^{-3} mol l^{-1} SASH solution in a total volume of 10 ml, was selected.

Effect of foreign ions

A systematic study of the interferences by foreign ions in the determination of Sc (100 ppb) was carried out. Various amounts of different ions were added, first testing a 4000-fold mass excess of interferent over scandium. If interference occurred, the ratio was reduced gradually until the interference ceased. The criterion for interference was fixed at a 5% variation of the average fluorescence intensity calculated for the established level of scandium. The results are given in Table 2.

Stoichiometry of the complex

The stoichiometry of the complex was studied under the established experimental conditions by the molar ratio and continuous variation methods.[15] The results obtained by both methods indicated that the composition of the complex was 1 : 1 (Sc^{3+} : SASH).

Analytical characteristics

Under the optimum experimental conditions, there was a linear relationship between the fluorescence intensity and scandium concentration in the range 0.43–100 ppb with a correlation coefficient (*r*) of 0.9987. The regression equation was $\Delta I_F = 146.28C$ (ng per 10 ml) − 1.837. The standard deviation of the fluorescence measurements was 0.063 obtained from a series of

Table 1 Influence of ethanol concentration on the difference in the fluorescence intensities (ΔI_F) of the Sc–SASH complex and reagent blank

Ethanol (% v/v)	25	30	35	40	50	55	60
ΔI_F	112.0	125.0	135.8	145.9	147.8	148.3	147.9

Table 2 Effect of foreign ions on the spectrofluorimetric determination of scandium (100 ppb) (tolerable error 5%)

Tolerance ratio (m/m)	Foreign ions
3000	SO_3^{2-}
1000	Ca^{2+}, Cd^{2+}, Mg^{2+}, ClO_4^-, Br^-, HCO_3^-, I^-, NO_3^-
100	Ba^{2+}, Pd^{2+}, $B_4O_7^{2-}$
50	Pb^{2+}
20	Hg^{2+}, V^V
10	Ag^+, Sr^{2+}, Zn^{2+}, Tl^{3+}, $Cr_2O_7^{2-}$, CrO_4^{2-}
5	MnO_4^-
4	Sn^{2+}, Cr^{3+}, Fe^{3+}
1	Be^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, HPO_4^{2-}, $H_2PO_4^-$, F^-

13 blank solutions. The limits of detection (k = 3) and of determination (k = 10) of the method were established according to the IUPAC definitions ($c_1 = kS_0/s$, where c_1 is the limit of detection, s_0 the standard error of blank determination, s the slope of the standard curve and k the constant related to the confidence interval)[16] and the values found were 0.13 and 0.43 ppb, respectively. The relative standard deviation was 1.1%, obtained from a series of 10 standards each containing 10 ppb of scandium. In Table 3, characteristics of the method are compared with those of similar published fluorescence methods for scandium determination.

Applications

The method was applied to the determination of scandium in geological soil samples. The procedure was as follows.

For the assay of scandium in geological soil samples, 0.5000 g of a fine powdered sample was weighed accurately into a platinum crucible, 1 g of boric acid, 5 g of sodium hydroxide and 10 drops of absolute ethanol were added to the sample and the mixture was heated in a muffle furnace at 560 °C for 60 min. The platinum dish was immersed in 6 mol l^{-1} hydrochloric acid, the fusion cake was transferred from the crucible into the acidic solution and left for 4–5 h to dissolve, then the solution was evaporated nearly to dryness in an electric furnace. The residue was dissolved in 20 ml of 6 mol l^{-1} hydrochloric acid and the solution was diluted to volume in a 50 ml calibrated flask, then filtered. A 40 ml aliquot was transferred into a beaker, about 100 mg of Ca^{2+}, 4 ml of hydrogen peroxide and 40 ml of 10% oxalic acid were added, then the solution was adjusted to pH 2 with aqueous ammonia (1 + 1), diluted to about 100 ml and heated at 75 °C for 1 min. After cooling and leaving for 30 min, the solution was filtered through a quantitative filter-paper and the beaker and the precipitate were washed with 1% oxalic acid three times. The precipitate and filter-paper were transferred into the original beaker, nitrated with 15 ml of concentrated nitric acid and 5 ml of perchloric acid and heated until fumes were evolved at high temperature. After cooling, 5 ml of 25% sulfosalicylic acid and a small amount of water to dissolve the residue were added, then a drop of Methyl Orange was added and the solution was neutralized with 15% sodium hydroxide solution until an orange color appeared, then 6 mol l^{-1} hydrochloric acid was added until a red color appeared. The solution was transferred into a separating funnel and the beaker was washed successively with 4 ml of 5% hydroxylamine hydrochloride, 4–5 ml of 1% formic acid and a small volume of water. The wash liquid was transferred into the funnel and diluted to about 30 ml with water. Scandium was extracted with 15 ml of 0.01 mol l^{-1} PMBP–benzene by shaking for 1.5 min. The aqueous layer was discarded and the extract was washed with three 5 ml portions of the wash liquid (the wash liquid was prepared as follows: first 20% sodium hydroxide solution was added to the solution containing 10 ml of 25% sulfosalicylic acid and one drop of Methyl Orange until the red color disappeared, 6 mol l^{-1} hydrochloric acid was added until a red color appeared, then 10 ml of 1% formic acid was added to the solution, which was subsequently diluted to 200 ml), then the extract was washed by shaking with two 5 ml portions of water (pH 3) for 15–20 s, discarding the aqueous layer. The scandium was stripped by shaking with two 10 ml portions of 4% hydrochloric acid for 1 and 0.5 min, respectively. The aqueous phases were combined in a beaker (the organic phases were discarded), then 0.1 g of sodium chloride was added and the mixture was evaporated nearly to dryness. The residue was dissolved in water and diluted to volume in a 50 ml calibrated flask. To 1.00 ml of this prior separated sample solution were added various amounts of standard scandium solutions and the scandium was then determined spectrofluorimetrically by the proposed method.

The standard additions method[20] was used in the analysis procedure. The results are given in Table 4 and show that after scandium had been extracted with PMBP–benzene, ions that had the same tolerance ratio as scandium did not interfere with its determination. The results were compared with the concentrations of scandium (Chinese Certified Reference Standard Value).

Table 4 Determination of scandium in geological soil samples (p = 0.95)

Sample*	Sc present (ppb)	Mean Sc found (ppb) (n = 6)	RSD (%)
15-GRD-31[a]	8.18	7.880 ± 0.11	1.17
15-GRD-38[b]	10.7	10.625 ± 0.09	1.35
15-GRD-41[c]	6.86	6.563 ± 0.10	1.76
15-GRD-45[d]	7.51	7.456 ± 0.09	1.43

* Other elements contents in samples (%): [a] Si 32.14, Na 2.89, Mg 1.21, K 0.93, Fe 2.39, Ca 3.25, Al 7.40, Zr 0.0243, Zn 0.00228, Y 0.00098, V 0.00551, Ti 0.1954, Rb 0.0031, Th, 0.00042, Sr 0.0532, Sm 0.00029, Pb 0.000803, P 0.0519, Ni 0.00512, Nb 0.000945, Mn 0.0365, Li 0.00096, La 0.00207, F 0.0266, Cu 0.00076, Cr 0.00839, Co 0.0010, Ce 0.0034, Ba 0.0472, B 0.0034, As 0.0098; [b] Si 32.10, Na 1.39, Mg 1.14, K 1.01, Fe 3.38, Ca 2.68, Al 5.04, Zr 0.0332, Zn 0.00491, Y 0.00188, V 0.00914, Ti 0.5299, Rb 0.00755, Th 0.00073, Sr 0.0283, Sm 0.00039, Pb 0.00152, P 0.0634, Ni 0.00542, Nb 0.00166, Mn 0.0562, Li 0.0019, La 0.00227, F 0.0293, Cu 0.00229, Cr 0.00115, Co 0.00182, Ce 0.0049, Ba 0.0544, B 0.00296, As 0.000593; [c] Si. 33.85, Na 2.72, Mg 0.58, K 1.32, Fe 2.71, Ca 1.42, Al 6.94, Zr 0.0154, Zn 0.0037, Y 0.00099, V 0.00622, Ti 0.2652, Rb 0.0052, Th 0.00044, Sr 0.0351, Sm 0.00023, Pb 0.0013, P 0.0356, Ni 0.00213, Nb 0.000777, Mn 0.0315, Li 0.00116, La 0.00168, F 0.0263, Cu 0.0016, Cr 0.00506, Co 0.0012, Ce 0.0026, Ba 0.0518, B 0.00069, As 0.000187; [d] Si 32.25, Na 2.68, Mg 0.68, K 3.84, Fe 3.58, Ca 1.59, Al 7.42, Zr 0.0324, Zn 0.00478, Y 0.00237, V 0.00993, Ti 0.4190, Rb 0.0151, Th 0.00273, Sr 0.0706, Sm 0.00075, Pb 0.00348, P 0.146, Ni 0.0011, Nb 0.00293, Mn 0.0586, Li 0.00080, La 0.00931, F 0.0563, Cu 0.00134, Cr 0.0027, Co 0.00112, Ce 0.0162, Ba 0.1795, B 0.0002, As 0.000132.

Table 3 Comparison of the characteristics of the proposed method with those published previously

Reagent*	λ_{ex}/nm	λ_{em}/nm	Extraction reagent	Sensitivity (ppb)	Major interferences	Ref.
Rhodamine B	563	578	Benzene	2	—	17
DH and UR	420	520	Benzene	16	—	18
HNS	405	445	Benzene-acetone	4	—	8
Morin and SDS	424	508		1.4	Al^{3+}, Ga^{3+}, Sn^{IV}, Fe^{3+}, Fe^{2+}, Ti^{III}, Nb^{IV}, Zr^{III}, F^-, EDTA	19
DPFH	387	492		5	Al^{3+}, Ga^{3+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, citrate, tartrate, oxalate	11
SABSH	388	465	PMBP–benzene	0.26		This work

* DH = 5,7-dinitro-8-hydroxyquinoline; UR = unsubstituted Rhodamine; HNS = 2-hydroxy-1-naphthaldehyde semicarbazone; SDS = sodium dodecyl sulfate; DPFH = di-2-pyridylketone-2-furoylhydrazone.

Conclusion

Several methods utilizing various organic reagents have been reported for the fluorimetric determination of scandium,[9–16] and in this work SASH was compared with these reagents and was shown to offer higher sensitivity (Table 3). The proposed highly sensitive method can be effectively used for the determination of trace amounts of scandium in geological soil samples.

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