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Microtitration of Sulfate with Beryllon II as Indicator: Determination of Sulfate in Environmental Samples

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With 3 Figures

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In recent years, acidity of atmospheric precipitation (rain and snow) has been found to be intimately linked with the presence of sulfate. While a number of approaches, including ion chromatography¹, are available for the determination of sulfate, simple and sensitive methods are scarce.

Microtitrimetric methods which employ a Ba²⁺ solution as titrant in a mixed aqueous solvent in the presence of a suitable indicator are well known²⁻¹⁸. While these methods are simple, sensitivities for applications to precipitation samples are marginal. Also at low sulfate levels, large positive errors result due to the presence of other ions. There is no clear consensus in the literature as to which of the large number of reported indicators provides the sharpest end point. Systematic studies for pertinent parameters (pH, solvent composition) have been reported for only one indicator-solvent system¹⁶.

In this work, the use of a new indicator, Beryllon II (also called DSNADNS, 2-(8-hydroxy-3,6-disulfo-1-naphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid) is presented. It provides improved sensitivity (0.25 ppm sulfate in the aqueous sample), negligible error due to co-anions, and sharper end point change and more optimum pH conditions than the indicators previously studied.

Experimental

Reagents and Equipment

Reagent grade chemicals were used in this study except for the indicators and 2-propanol. The latter was solvent grade; no difference in titration blanks or other parameters were found with purified distilled solvent. Indicator dyes and dye intermediates were obtained either from Aldrich Chemical Co. (Milwaukee, WI) or Pfaltz and Bauer Inc. (Stamford, CT). Dye purity was examined by thin layer chromatography (tlc) on silica gel plates using three different binary solvent systems. No significant impurities were found in Thorin and Sulfonazo III, while Fast Sulfon Black F contained a minor second component. The purity of Beryllon II differed widely from batch to batch. Since initial studies with this indicator proved promising, the pure dye was synthesized according to literature procedure¹⁹ as follows.

H-acid (1-amino-8-hydroxy-3,6-naphthalene disulfonic acid) and chromotropic acid (1,8-dihydroxy-2,7-naphthalene disulfonic acid) were recrystallized from hot water. The H-acid (3.8 g) was put in 50 ml of water, 2 ml of conc. HCl was added and the suspension was warmed to 35°. Sodium nitrate (0.7 g in 15 ml of water) was next added and the diazotization reaction was allowed to proceed at 30–35° for 15 min. The mixture was then cooled to room temperature (~25°), and chromotropic acid (4 g) and sodium acetate (5 g) dissolved together in 60 ml of water were added to the mixture. During the course of the coupling reaction, the mixture turned violet with eventual separation of brown dye crystals. After 6 hr, the reaction mixture was filtered, the solid residue was dissolved in 150 ml of hot water and the solution was filtered again to remove any turbidity. Conc. HCl (50 ml) was then added to the filtrate which was allowed to cool slowly. The resulting violet-brown platelets of Beryllon II was collected on a filter, washed with dilute HCl (3 M) and dried at 110°. The purity of the product was checked by TLC; only one component was found.

For BaSO₄ solubility studies, 50% aqueous (v/v) organic solvents were deionized by ion exchange. BaSO₄ solubility was determined by equilibrating the pure compound with 25 ml of solvent (48 h with mechanical shaking at 50°, followed by 24 h at 25°), filtering through a 0.1- μ m membrane filter, evaporating the solvent, dissolving the residue in alkaline (KOH) EDTA solution, and measuring the barium in the resulting solution by atomic absorption spectrometry (N₂O–C₂H₂ flame, Perkin-Elmer model 2380 instrument) in comparison to BaSO₄ standards dissolved in alkaline EDTA solution.

For ion chromatographic analysis, the sample was filtered through a 0.45- μ m membrane filter and then passed through analytical grade cation exchange resin in H⁺-form. 100 μ l of the sample was injected on Dionex anion separator columns (3 \times 150 mm precolumn + 3 \times 250 mm separator column, Dionex Corporation, Sunnyvale, CA), with the standard eluent flowing at 2 ml/min.

Solubility of the barium-dyes salts in 80% 2-propanol were determined by measuring the optical absorption due to the dye in a membrane-filtered, saturated solution of the salt at the dye absorption maximum and compared to the results obtained with standard solutions of the dye in the same solvent.

The pH values reported in this paper were measured with an electrode calibrated with aqueous buffers and are therefore apparent pH values.

Titration Procedure

Filter sample (preferably through a 0.45- μm membrane filter) to remove all suspended impurities and pass the filtrate through a washed H^+ -form cation exchanger column, discarding the first few ml of effluent. A small ion exchange column, made from a pasteur pipet with a glass wool plug is adequate. To 4 ml of the ion-exchanged sample add 16 ml of 2-propanol and adjust the pH to 3.5 with 0.2 M NaOH or 0.2 M HClO_4 (each in 80% 2-propanol). Add 3–4 drops (150–200 μl) of aqueous 0.1% indicator and titrate with 0.005 M $\text{Ba}(\text{ClO}_4)_2$ in 80% 2-propanol. The titrant may be standardized by gravimetry or as described in the literature¹⁶. At the end point, the color of the solution changes from deep purple to pale brown-pink, which is easily visually perceived. Determine the titer of a blank in the same fashion and subtract from sample titers. The use of a 5-ml microburet and a base illuminated magnetic stirrer will facilitate trace level determinations.

Results and Discussion

Choice of titration medium. In 50% methanol, ethanol, 2-propanol, acetone, 1,4-dioxane, and acetonitrile, we found the solubilities of BaSO_4 to be 0.86, 0.58, 0.64, 0.73, 0.80, and 1.40 μM respectively. These values are the mean of triplicate measurements with 5–7% relative standard deviation and are lower than equilibrium values. Complete attainment of equilibrium appears to require more than 10 days. With identical methodology, aqueous solubility was found to be 80 μM , 20% lower than the literature value^{20, 21}. Since the solubility observed during a titration, albeit different from equilibrium solubility, may be expected to follow the same relative order among the various solvents studied above, these data were used for selecting the titration medium. The solubility difference among solvent systems involving ethanol, 2-propanol or acetone is marginal and there is no significant cost advantage for any given solvent. We chose 2-propanol for further studies because of its lowest vola-

tility among these three and thus minimize changes in titrant concentration or medium composition during a titration. Various ratios of 2-propanol: water were investigated, 80% 2-propanol was found to be optimum.

Choice of indicator. Indicators used in previous studies include Alizarin Red S^{2,3}, Carboxy-arsenazo^{4,6}, Arsenazo III^{7,8}, Sulfonazo III^{4,7,9,10}, Dibromosulfonazo III⁴, Chlorophosphonazo III¹⁴, Orthani^{7,8,11}, Nichromazo⁴, Dimethylsulfonazo III⁴, Stilbnaphthazo¹⁸ and Thorin^{16,17}. With the exception of the first, all these dyes bear the 2,7-naphthalenedisulfonate functionality or are sterically equivalent. The indicator behavior of such dyes has been interpreted in terms of complexation by substituent groups attached to the chromotropic acid nucleus^{7,10}. Whether the adsorption of the dye on BaSO₄ in the presence of excess Ba is promoted primarily by surface complexation or surface precipitation has not received much attention, unlike the analogous case of silver halide titrations where dominant mode of action for many indicators are well characterized²². A low solubility of the Ba-dye salt is expected to promote the role of surface precipitation in indicator behavior, which explains the success of Thorin as indicator. A very high stability constant for the Ba-dye adduct is not necessarily useful since it leads to premature indication of endpoint, as with Chlorophosphonazo III and Methylthymol blue. A number of dyes, all derivatives of chromotropic acid (Chromotrope 2R, Chromotrope 2B, SPADNS, DISNADNS, Nitroso-R-salt, Calcichrome, Gallion, Fast Sulfon Black F and Beryllon II) (see the monograph in Ref. 22 for structures), were screened for indicator behavior with barium and solubility of the Ba-dye salt and all showed some adsorption on BaSO₄ in the presence of excess Ba. In addition, the last four dyes exhibited discernible color changes in the presence of Ba. These four were studied further along with the established indicators, Alizarin Red S, Arsenazo III, Sulfonazo III and Thorin under realistic titration conditions (100 ppm SO₄²⁻) in 80% 2-propanol medium at apparent pH values from 3–12. Discernible color changes were observed for Alizarin Red S (pH 4–9), Arsenazo III (pH 8), Beryllon II (pH 3–11), Fast Sulfon Black F (pH 3–9), Sulfonazo III (pH 3–12) and Thorin (pH 3–10). Further studies on sharpness of color change and titration error limited this choice to Thorin and Beryllon II, especially for trace sulfate levels (10 ppm). For both of these indicators, optimum solvent composition and apparent pH was found to be 80% 2-PrOH and 3.5 respectively, in agreement with the previously recommended value for Thorin¹⁶. The results of a comparative study of Thorin and Beryllon II as indicators are presented in Table I. While the

difference is minor at higher concentrations, the superiority of Beryllon II at very low sulfate concentrations is clear.

Table I. Comparison of Beryllon II and Thorin as Indicator

Sulfate taken, ppm	Sulfate found, ppm (triplicate determinations)	
	Thorin	Beryllon II
54.3	53.2 ± 0.55	54.4 ± 0.14
27.2	26.0 ± 0.14	26.9 ± 0.14
13.6	13.2 ± 0.14	13.2 ± 0.14
5.43	5.2 ± 0.14	5.3 ± 0.07
2.72	2.5 ± 0.14	2.7 ± 0.07
1.09	0.56 ± 0.09	1.09 ± 0.00
0.54	0.0	0.54 ± 0.07

Titration conditions: 4 ml of aqueous sulfate standard + 16 ml of 2-propanol + 3—4 drops of 0.1% aqueous indicator, pH adjusted to 3.5, 0.005 M Ba(ClO₄)₂ (in 80% 2-propanol titrant).

Studies with environmental samples. Precipitation samples (snow/rain) and water samples from several local lakes were collected for parallel sulfate determinations by microtitration with Beryllon II as indicator and by ion chromatography. Cations were removed by prior ion-exchange to prevent negative interferences due to the formation of metal-indicator complexes¹⁷. The results are presented in Table II; the two methods exhibit good agreement.

Table II. Results with Environmental Samples

Sample type	Sulfate (ppm) (± S. D.) (triplicate determinations)	
	Beryllon II	Ion chromatography
Snow sample 1	0.26 ± 0.15	0.26
Snow sample 2	0.26 ± 0.15	0.25
Rain sample 1	0.77 ± 0.15	0.76
Lake 1	288 ± 0.0	277
Lake 2	329 ± 0.0	313
Lake 3	12.9 ± 1.85	13.2
Lake 4	11.6 ± 0.0	10.5

Beryllon II as indicator: spectrophotometric studies. In the past, discordant claims have been made as to the superiority of different indicators with respect to sharpness of color change. For example,

Thorin was found superior to Alizarin Red S¹⁷, Sulfonazo III was found better than Thorin and Dimethylsulfonazo III better than Sulfonazo III⁴. We found Thorin to be the most suitable among previously used indicators. In the following paragraphs we present the spectrophotometric evidence for the superior performance of Beryllon II (Fig. 1) at various stages of titration. In each case, the three separate spectra represent three stages: prior to addition of titrant, shortly before the theoretical equivalence point, and shortly after the theoretical equivalence point, under identical conditions (50 ppm SO_4^{2-} in 80% 2-propanol, pH 3.5, 0.005 M $\text{Ba}(\text{ClO}_4)_2$ titrant, 4 drops 0.1% indicator). As these spectra indicate, the end point is much easier to detect visually with Beryllon II as indicator compared to Thorin.

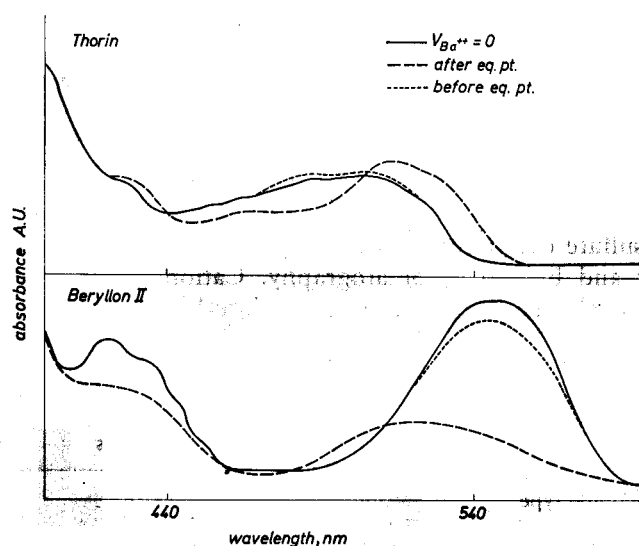


Fig. 1. Spectra of Thorin and Beryllon II at various stages of titration

The absolute solubility of the Ba-dye salt is a key parameter in determining the lowest concentration of sulfate that can be successfully titrated as well as in controlling the degree of interference from co-anions (which may have an affinity for Ba and thus cause anomalously high results¹⁷). The solubilities of the barium salts of Beryllon II, Fast Sulfon Black F, Sulfonazo III and Thorin were determined in 80% 2-propanol at a pH of 3.5 and found to be 0.265, 2.57, 3.76 and 3.47 μM respectively. The lower solubility of Ba-Beryllon II accounts for the applicability of Beryllon II to titrations

of very dilute sulfate solutions where Thorin fails totally. The color change at the equivalent point in precipitation titration require finite time and the color change is faster with Beryllon II, compared to Thorin. Fast Sulfon Black F is similar in structure to Beryllon II and leads to a highly insoluble salt; however, the color change at the end point is poor.

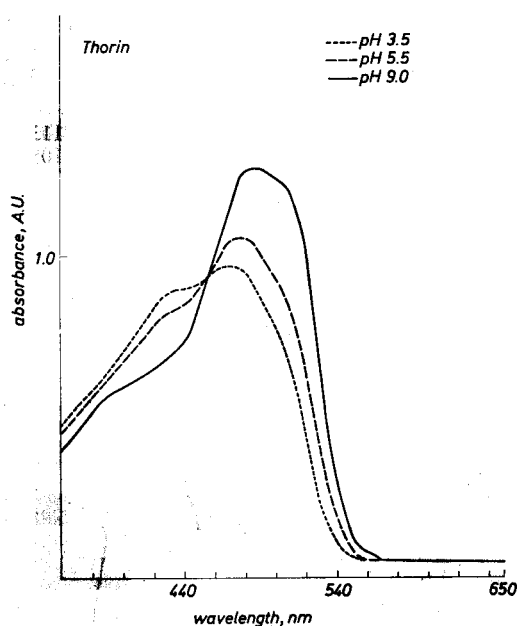


Fig. 2. Spectra of Thorin as a function of pH

Another significant advantage of Beryllon II over Thorin is applicability over a broader pH range. The spectra of Thorin and Beryllon II are shown in Figs. 2 and 3 respectively as a function of pH. The pH dependence of Thorin originates from the weakly ionized arsonic acid functionality present in Thorin as opposed to Beryllon II which contains only sulfonic acid groups. The change in the spectral behavior of Beryllon II at very high pH is presumably due to the ionization of the naphtholic hydrogen(s). While Beryllon II does behave as a useful indicator over a large pH range (2—9), it should be noted that utilization at a pH level substantially higher than the recommended value of 3.5 involves a greater potential of interferences from protolyzable anions (e. g. phosphate.)

Finally, the effects of potentially interfering co-anions need to be addressed. With prior cation-exchange, at realistic levels (see Table III) no statistically significant interference was observed. Ta-

Table III. Effects of Other Anions on Sulfate Determination

Compound added	Sulfate taken 10^{-9} mol	Co-anion/Sulfate mole ratio	Sulfate found (\pm S. D. $n=3$) 10^{-9} mol
NaCl	113	60	113 ± 2.9
	113	115	113 ± 2.9
NaF	113	70	113 ± 7.7
	113	140	108 ± 2.9
NaH ₂ PO ₄	113	5	113 ± 2.9
	113	10	108 ± 5.8
	113	20	103 ± 0.0
NaNO ₃	226	2	221 ± 2.9
	226	6	216 ± 0.0
	226	10	211 ± 2.9

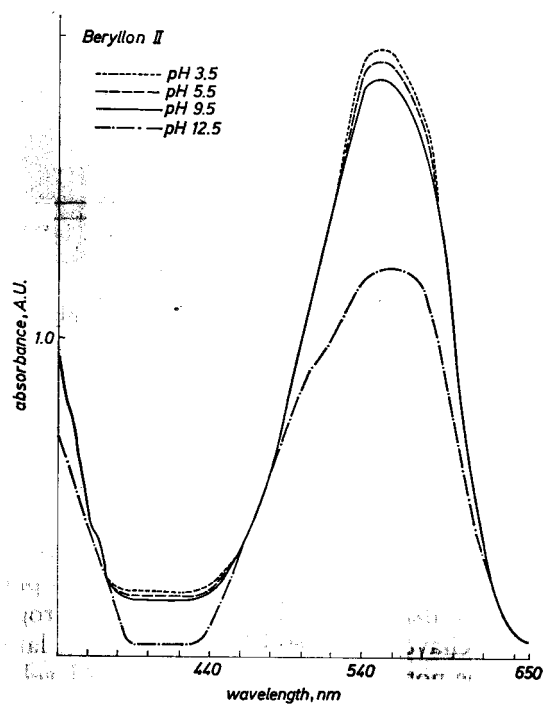


Fig. 3. Spectra of Beryllon II as a function of pH

ble III shows the results without prior cation exchange and with all anions being present as the sodium salt. Beryllon II reacts with high concentrations of sodium and more so with potassium (but not with lithium or ammonium) and the small negative interferences observed are actually due to the presence of sodium. Note that the extent of interference increases with decreasing ion pairing between the anion and the sodium ion. Prior cation-exchange is absolutely essential if metal ions other than the above mentioned are present. The complete lack of anion interference in cation exchanged samples is remarkable; a comparison with past work with other indicators¹⁹ will reveal that this is in marked contrast, especially for phosphate.

In conclusion, the method presented here is a sensitive and precise method for the determination of trace sulfate which can be carried out with a minimum of equipment.

Summary

Microtitration of Sulfate with Beryllon II as Indicator: Determination of Sulfate in Environmental Samples

A new indicator, 2-(8-hydroxy-3,6-disulfo-1-naphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Beryllon II, DSNADNS) is proposed for microtitrimetric determination of sulfate with barium. This method is an order of magnitude more sensitive (LOD 0.25 ppm) and has less interference than the existing indicators. The color change is sharper and faster compared to Thorin. Titration is carried out in 80% 2-propanol at an apparent pH of 3.5. The superiority of the indicator is attributed to the lower solubility of the barium-dye salt. Results are presented for environmental samples and compared with values obtained by ion chromatography.

Zusammenfassung

Mikrotitration von Sulfat mit Beryllon II als Indikator: Bestimmung von Sulfat in Umweltproben

Als neuer Indikator für die Bestimmung von Sulfat mit Barium wurde 2-(8-Hydroxy-3,6-disulfo-1-naphthylazo)-1,8-dihydroxynaphthalin-3,6-disulfonsäure (Beryllon II, DSNADNS) vorgeschlagen. Das Verfahren ist um eine Größenordnung empfindlicher und wird weniger gestört als bei Verwendung üblicher Indikatoren. Der Farbwechsel ist schärfer und rascher als mit Thorin. Die Titration erfolgt in 80% 2-Propanol bei pH 3,5. Die Überlegenheit des vorgeschlagenen Indikators dürfte der geringeren Löslichkeit seines Bariumsalzes zuzuschreiben sein. Ergebnisse für Umweltproben wurden mit den Werten der Ionenchromatographie verglichen.

References

- ¹ E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.), *Ion Chromatographic Analysis of Environmental Pollutants*. Vol. I. Ann Arbor: Ann Arbor Science. 1978.
- ² L. de Zombory, *Z. anorg. allgem. Chem.* **184**, 237 (1929).
- ³ J. S. Fritz and M. Q. Freeland, *Analyt. Chemistry* **26**, 1593 (1954).
- ⁴ B. Budesinski and L. Krumlova, *Analyt. Chim. Acta* **39**, 375 (1967).
- ⁵ K. F. Novikova, N. N. Basargin, and M. F. Tsyganova, *Zh. Anal. Khim.* **16**, 348 (1961).
- ⁶ A. A. Nogina and G. G. Kobayak, *Uch. Zap., Permsk. Gos. Univ.* **25**, 73 (1963).
- ⁷ S. B. Savin, M. Dedkov, and V. P. Makarova, *Zh. Anal. Khim.* **17**, 43 (1964).
- ⁸ Z. K. Karalova and N. P. Shibaeva, *Zh. Anal. Khim.* **19**, 258 (1964).
- ⁹ B. Budesinski, *Analyt. Chemistry* **37**, 1159 (1965).
- ¹⁰ B. Budesinski and D. Vrazalova, *Z. analyt. Chem.* **210**, 161 (1965).
- ¹¹ S. B. Savin, T. G. Akimova, V. P. Dedkov, and G. M. Varshal, *Zh. Anal. Khim.* **24**, 1868 (1969).
- ¹² V. I. Kuznetsov and N. N. Basargin, *Zavod. lab.* **31**, 538 (1965).
- ¹³ N. N. Basargin and A. A. Nogina, *Zh. Anal. Khim.* **22**, 394 (1967).
- ¹⁴ B. Budesinski, *Microchem. J.* **14**, 242 (1969).
- ¹⁵ R. S. Fiedler and C. H. Morgan, *Analyt. Chim. Acta* **23**, 538 (1960).
- ¹⁶ J. C. Haartz, P. M. Eller, and R. W. Hornung, *Analyt. Chemistry* **51**, 2293 (1979).
- ¹⁷ J. S. Fritz and S. S. Yamamura, *Analyt. Chemistry* **27**, 1461 (1955).
- ¹⁸ L. V. Markova, *Ukrain. Khim. Zhur.* **23**, 89 (1957).
- ¹⁹ A. M. Lukin and G. B. Zavarikhina, *Zh. Anal. Khim.* **11**, 393 (1956).
- ²⁰ T. C. Gupta and A. K. Bhattacharya, *Z. analyt. Chem.* **161**, 321 (1957).
- ²¹ K. H. Lieser, *Z. anorg. allgem. Chem.* **355**, 225 (1965).
- ²² E. Pungor and E. Schulek, in: E. Bishop (ed.), *Indicators*. Oxford: Pergamon. 1972.

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