

Quantification of sulfur from organic and inorganic materials for determination of ^{35}S

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^{35}S 측정을 위한 유기물과 무기물에서 황의 정량

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요 약: 산 매질 조건에서 다양한 할로겐산화물을 이용하여 황 원소를 포함한 유기물(thiourea, methionine)과 무기물(sulfate, thiophosphate)의 산화에 관한 연구를 수행하였다. 산화반응의 최적조건은 3 M 질산용액 매질에서 bromate (BrO_3^-)를 산화제로 사용했을 때 얻어졌다. 유기 황 화합물인 thiourea에서는 100%의 산화 수율을 확인하였으며, methionine을 사용한 결과는 87%이었다. 또한 무기 황 화합물인 thiophosphate와 sulfate의 산화는 각각 80%와 100%의 산화 수율을 얻었으며, 5%의 상대표준표차(RSD)가 있음을 확인하였다. Thiourea의 산화는 1.6배의 bromate가 필요하였으며, methionine과 thiophosphate의 경우에는 20배 이상이 필요함을 관찰하였다. 황산염 이온은 황산 바륨(BaSO_4)으로 침전을 확보하였으며, 이때 얻어진 방사성 황산 바륨($\text{Ba}^{35}\text{SO}_4$)은 기체비례계수기(gas proportional counter, GPC)를 이용하여 정량적으로 측정하였다. ^{35}S 측정을 위한 소광보정곡선은 무게 차이를 이용하여 작성되었다.

Abstract: The oxidation studies of a sulfur to a sulfate ion by various oxyhalide oxidants in organic (thiourea, methionine) and inorganic (sulfate, thiophosphate) compounds were carried out in an acidic solution. The optimized result of the oxidation reaction was obtained when a bromate compound (BrO_3^-) as an oxidant and a 3 M HNO_3 solvent were used. The chemical yield for the oxidation of the organic and inorganic sulfur compounds to a sulfate ion was monitored as 80% for thiophosphate, 87% for methionine, and 100% for thiourea and sulfate within 5% RSD. The oxidations of thiourea required at least 1.6 equivalents of the bromate in an acidic solution. In the case of the oxidation of methionine and thiophosphate, the oxidation yields were above 80% if the bromate was used at 20 times higher than that of the substrates. The sulfate ion was quantitatively measured by using a GPC counting of ^{35}S followed by precipitates of BaSO_4 . A quenching correction curve for the ^{35}S counting was obtained to use the difference via the precipitate weight result.

Key words : ^{35}S , oxidation, thiourea, methionine, sulfate, thiophosphate, GPC

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1. Introduction

Natural sulfur consists of four stable isotopes. The main isotopes are ^{32}S (95.02%) and ^{34}S (4.21%). Beside the stable isotopes, there also exists a radioactive one ^{35}S ($T_{1/2}=87.4$ d, $E_{\text{max}}=167$ keV, pure β^- emitter). ^{35}S is one of the cosmogenic radionuclide generated by cosmic rays through a spallation of argon atoms. ^{35}S for a labeled compound such as ^{35}S -thiourea is produced from a pile irradiation of neutron ($^{35}\text{Cl}(n,p)^{35}\text{S}$).¹ Most ^{35}S produced by cosmic rays is rapidly converted to sulfur dioxide (SO_2) and sulfate (SO_4^{2-}), and attached onto ambient aerosols.

^{35}S -sulfate has been used as the precursor for the biosynthesis of amino acids (^{35}S -methionine, ^{35}S -cysteine, etc).^{2,3} ^{35}S -thiourea was studied for an autographic image enhancement.⁴ The derivatives of ^{35}S -thiourea have been applied to therapeutic antithyroid drugs.^{5,6} Vitvisky *et al.* reported results on the incubation of mouse and human neurons and astrocytes in a medium with ^{35}S -methionine.⁷ The anatomical distribution of [^{35}S]dATPgS (2'-deoxyadenosine 5'-O-(1- ^{35}S)thio)triphosphate) binding sites in the brain and spinal cord was examined using in vitro autoradiography.⁸

The quantities of ^{35}S do not present a significant external exposure hazard since the low-energy emissions barely penetrate the outer dead layer of the skin. For uptakes of inorganic sulfur, 15% is assumed to be retained with a 20 day biological half-life and 5% retained with a 2,000 day biological half-life. The remaining 80% is assumed to be rapidly excreted. Because of its relatively weak emission, ^{35}S is primarily an internal radiation hazard. TLDs and Geiger-Müller detectors are not effective because the former does not detect ^{35}S and the latter is measured to a low efficiency ($\sim 10\%$) for detecting ^{35}S . Therefore, it is important to use it through a careful handling and frequent monitoring, either with survey meters with thin-window probes or by taking wipe samples and counting them in a gas proportional counter (GPC) and/or a liquid scintillation counter (LSC).

The analysis of ^{35}S can be performed by using the following methods, a paper chromatography, an ignition, and a gravimetric method. Vercier and Raggenbass reported that the samples of aqueous and organic solvents separated from paper chromatographic columns were detectable by a Geiger-Müller counter (counting efficiency; ~ 0.1).⁹ Barakat and Zahran studied a comparison between a flow monitoring counter (counting efficiency; ~ 1) and a LSC (counting efficiency; 0.67) for organic materials.¹⁰ After the ignition of organic materials, the flow monitoring counter gave a high yield ($\sim 100\%$). But this method used only at below 10 mg of the ignition samples and the interferers such as ^{14}C , ^{32}P were not separated. After the separation of ^{35}S to the resin from the seawater¹¹ or rainwater,¹² insoluble barium sulfate was then precipitated. The precipitate separated from the seawater was fused with Na_2CO_3 and the fusion product was soluble in water. Another from rainwater was filtered with a GF/B filter and this was soluble in a cocktail (Ultima-Gold LLT). Then the aqueous solutions mixed with scintillation cocktails were counted by LSC.

In this study, inactive sulfur compounds such as thiourea, DL-methionine, and thiophosphate were oxidized to sulfate ions by using oxyhalide as an oxidant for the separation and the analysis of the wastes generated from the institution. And we need to use many quantities (<10 g) of samples and acquire adequate counting efficiency. This sulfate ion was quantitatively measured by a gravimetric method.^{11,12} On the basis of the oxidation, a labeled sulfur compound such as $\text{Na}_2^{35}\text{SO}_4$ would be appropriate for the examination of a chemical yield.

2. Experimental

2.1. Reagents and equipment

Thiourea (NH_2CSNH_2), DL-methionine ($\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$), and thiophosphate, disodium salt (Na_2HSPO_3) as the compounds containing a sulfur were obtained from Aldrich Co. Sodium chlorate (NaClO_3), sodium bromate (NaBrO_3), and potassium iodate (NaIO_3) as an oxidant were purchased from Junsei Chemical

Co. Sodium perchlorate (NaClO_4), sodium periodate (NaIO_4), and sodium hypochlorite (NaOCl) were obtained from Aldrich Co. Sodium sulfate (Na_2SO_4) as a carrier and barium chloride (BaCl_2) as a coprecipitate were purchased from Wako Chemical Co. Hydrochloric acid (HCl) of 32% and nitric acid (HNO_3) of 65% were purchased from Merck Co. All the chemicals were used as received and as an aqueous solution. The radioactive standard solution $\text{H}_2^{35}\text{SO}_4$ in H_2O (425 kBq/g, Oct. 5, 2007) purchased from North American Scientific Co. was diluted to a concentration of 4.25 kBq/mL.

The counting of ^{35}S was recorded on a Canberra S5-XLB gas proportional counter and adjusted by a quenching correction curve via the weight of barium sulfate.

2.2. Quantification of the sulfate ion

One mL of 70 mM sodium sulfate solution was added into a centrifuge tube. One mL of 4 M HCl for an acidic condition was added to the solution, and 2 mL of 0.1 M BaCl_2 (aq) was utilized as a precipitant of BaSO_4 . After washing with deionized water three times, BaSO_4 precipitates were dried by an IR lamp and weighed.

2.3. Oxidation of the sulfur in thiourea

One mL of 0.1 M thiourea solution was added into a centrifuge tube. After 1 mL of 4 M HCl and 1 mL of various 0.2 M oxidants (NaOCl , NaClO_3 , NaBrO_3 , NaIO_3 , NaClO_4 , and NaIO_4) were added to the solution, it was shaken vigorously. And 2 mL of 0.1 M BaCl_2 (aq) was inserted as a precipitant of BaSO_4 . After washing with deionized water three times, BaSO_4 was dried by an IR lamp and weighed.

2.4. Oxidation of methionine and thiophosphate

One mL of 0.1 M methionine or thiophosphate and 1 mL of 70 mM sodium sulfate solution as a carrier were added into a round bottom flask. Two mL of 0.67 M NaBrO_3 was added and 50 mL of 3 M HNO_3 was slowly added dropwise by a dropping funnel. After refluxing for 3 h the sample was

filtered and the precipitate and/or by-product were removed. And the filtrate was evaporated by an IR-lamp and the dried sample was dissolved in 5 mL of 4 M HCl . After washing the dried sample two times, 2 mL of 0.1 M BaCl_2 as a coprecipitate was added. After washing with deionized water three times, BaSO_4 was dried by an IR lamp and weighed.

2.5. Quenching correction curve for a GPC counting of ^{35}S

Six centrifuge tubes containing 0.2-1.5 mL of 70 mM Na_2SO_4 were prepared. 0.1 mL of $\text{H}_2^{35}\text{SO}_4$ in H_2O (586 Bq/mL) was inserted in those samples. After the insertion of 0.1 M BaCl_2 , precipitated BaSO_4 was separated by a centrifuge. This was transferred to a copper planchet weighed in advance. Those samples were counted by GPC for 50 min. Quenching correction curve was drawn for the counted values and the weight of the precipitated BaSO_4 .

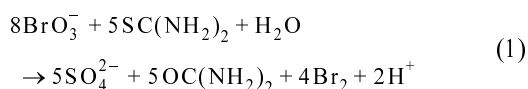
2.6. Recovery test for $\text{H}_2^{35}\text{SO}_4$

The recovery test for $\text{H}_2^{35}\text{SO}_4$ was performed by measuring the weight and the counting efficiency of GPC. 0.5 mL of 70 mM Na_2SO_4 and 0.1 mL of $\text{H}_2^{35}\text{SO}_4$ in H_2O (335 Bq/mL) were inserted in the flask. 2 mL of 0.67 M NaBrO_3 was added and 50 mL of 3 M HNO_3 was added dropwise by a dropping funnel. After a refluxing for 3 hr, the sample was filtered and the precipitate and/or by-product were removed. And the filtrate was evaporated by an IR-lamp and the dried sample was dissolved in 5 mL of 4 M HCl . After washing the dried sample two times, 2 mL of 0.1 M BaCl_2 as a coprecipitate was added. After washing with deionized water three times, BaSO_4 was dried by an IR lamp and weighed. And the samples were counted by a GPC for 30 min and adjusted by a quenching correction curve.

3. Results and Discussion

3.1. Determination of sulfur in thiourea

In case of free thiourea, the carrier (Na_2SO_4) was converted to a barium sulfate of around 100% with a 2.5% error tolerance.



As shown in Eq. (1), thiourea was transformed to urea by the oxidant, bromate. Also a sulfate ion and bromine were formed through the oxidation-reduction reaction in an acidic solution, respectively. The insoluble barium sulfate was then precipitated with the addition of aqueous BaCl_2 to the solution. The oxidation of thiourea (0.1 mmol) to sulfate required at least a 1.6 equivalent of the bromate ion (Eq. 1). Then thiourea was sufficiently oxidized at twice the amount of the bromate ions (NaBrO_3 : 0.2 mmol).¹³

The oxidation of the sulfur in thiourea by various oxyhalides oxidants in an acidic solution was observed by using a gravimetric method (Table 1). Chlorate (ClO_3^-) and perchlorate (ClO_4^-) as oxidants oxidized a thiourea to a sulfate ion via no precipitate. In the case of the iodate (IO_3^-) and periodate (IO_4^-) oxidants, the yield was over 100% because of the precipitate of barium sulfate as well as the barium iodate ($K_{\text{sp}}=4.01 \times 10^{-9}$) and barium periodate, respectively. The yield of the iodate was observed near 100%. The result for bromate as an oxidant was in the vicinity of 100%.

3.1. Determination of Sulfur in methionine and thiophosphate

Unlike thiourea, methionine and thiophosphate were not easily oxidized to a sulfate ion because

Table 1. The oxidation of a sulfur in a thiourea by various oxidants in an acidic solution

HCl concentration	Oxidant	%Yield
1 M	Bromate (BrO_3^-)	98.2±1.5
2 M		102±1
4 M		103±3
4 M	Chlorate (ClO_3^-) Perchlorate (ClO_4^-)	No reaction
1 M	Iodate (IO_3^-)	167±2
2 M		143±7
4 M		102±4
4 M	Periodate (IO_4^-)	115±1
4 M	HOCl	85.5±0.4

Table 2. The oxidation of DL-methionine and thiophosphate by sodium bromate

Substrate (mmol)	NaBrO_3 (mmol)	Recovery (%)	
		Methionine	Thiophosphate
0.1	0.2	-	-
0.1	0.4	-	-
0.1	0.6	-	12.7
0.1	1.0	12.7	61.4
0.1	1.4	17.0	65.2
0.1	2.0	87.1	80.2
0.1	3.3	66.8	77.0
0.1	6.6	12.2	64.1
0.1	33.1	-	48.0

methionine is a stable sulfide and a phosphorous binding with sulfur in a thiophosphate is closer than oxygen from the principle of the hard-soft acid-base theory. Then the condition was changed to 3 M HNO_3 for a more vigorous oxidation. As shown Table 2 in the condition of 0.1 mmol of a substrate, the mole number of NaBrO_3 as an oxidant was changed from 0.2 to 33.1 mmol. The more the amount of NaBrO_3 was increased to 2.0 mmol, the more the yield of the oxidation was increased to about 80%. But the yield was decreased at over 6.6 mmol because NaBrO_3 was spontaneously decomposed into the bromine and oxygen in an acidic condition.

3.2. Counting of ^{35}S by GPC

Because ^{35}S is pure β^- emitter and GPC can determine β^- emitting into the sample surface, the

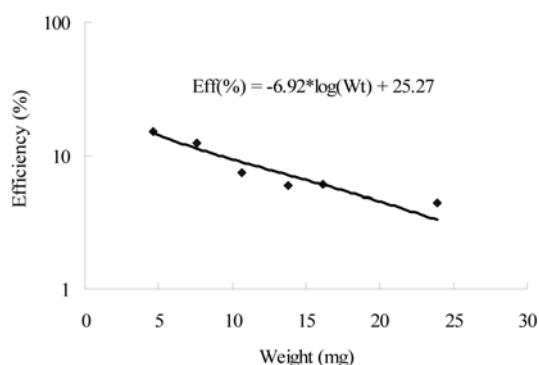


Fig. 1. The quenching correction curve for counting efficiency via the weight of $\text{Ba}^{35}\text{SO}_4$.

Table 3. Counts and efficiency for ^{35}S standard sample by GPC adjusted with the correction curve

Counts (cpm)	Efficiency (%)
219.22	10.91
234.92	11.69
213.52	10.63
223.52	11.13
221.42	11.02
215.72	10.74
221.39 \pm 7.57	11.02 \pm 0.38

counting must consider the weight of the sample supplementing the surface thickness. To prepare the quenching correction curve, the BaSO_4 precipitate's variable weight was counted by GPC for 50 min. The counting efficiency (ϵ) was observed as 15-4%. The correction curve via a weight is depicted in Fig. 1. This curve was used for the adjustment for the activity of ^{35}S . In the base on this correction curve, the counting efficiency (ϵ) for the recovery test of ^{35}S (33.48 Bq) was measured as 11.08 \pm 0.35% (Table 3) and the recovery efficiency was 99.42 \pm 0.27%.

4. Conclusions

The determination of ^{35}S was carried out by a gravimetric method. The oxidation of thiourea required at least 1.6 equivalents of the bromate compound (BrO_3^-) in an acidic solution. An oxidant for the oxidations of methionine and thiophosphate needs to be 20-fold moles and the conversion yield at the sulfates was 87% and 80%, respectively.

The quenching correction curve for ^{35}S by GPC was established and adjusted for the counting of a sample separated from a radioisotope.

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