

Quantification of Sulfur by the Wet Oxidation for the Determination of ^{35}S

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1. Introduction

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

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 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 are not effective and Geiger-Müller detectors can measure to low efficiency (~10%) for detecting ^{35}S . Therefore, it is important to use careful handling and frequent monitoring, either with survey meters with thin-windows probes or by taking wipe samples and counting in a liquid scintillation counter (LSC).

The anatomical distribution of [^{35}S]dATP alpha S binding sites in the brain and spinal cord was examined using in vitro autoradiography. The binding sites showed a widespread distribution throughout the brain and spinal cord.

The analysis of ^{35}S was kwon three methods, chromatographic columns by means of Geiger-Müller counter (counting efficiency; ~0.1), the ignition of the samples by LSC (counting efficiency; 0.65), and the oxidation of the sulfur site by the oxidant (bromate) (counting efficiency; 0.85).

In this study, inactive sulfur compound, such as thiourea, was oxidized to sulfate ion by the oxidant. This sulfate ion was quantitatively measured by the gravity method. On the basis of the oxidation, labeled sulfur compounds such as ^{35}S -thiourea and [^{35}S]-dATP were applied. And the analysis of DAWs (dry active wates) such as syringe, glove, and/or paper could be applied by the oxidation method.

2. Experiments and Result

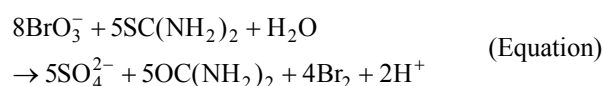
2.1. Reagents

Thiourea as sulfur compound and sodium bromate as the oxidant were purchase from Junsei Chemical Co. Sodium nitrate and barium chloride as the coprecipitate were obtained from Wako Chemical Co. HCl of 32% of the concentration was purchased from Merck Co. All chemicals were used as received and aqueous solution.

2.2. Experiment

10-100 μL of 0.1 M thiourea and same volume of 0.2 M sodium bromate were mixed in the centrifuge tube, respectively. After inserted the addition of 1 mL of 4 M HCl as the reaction promoter, aqueous solution was vigorously shaken by using a voltex-mixer. The solution changed to yellow color was mixed with 1 mL of 7.04 mM Na_2SO_4 as the carrier. After stirring, 2 mL of 1 M BaCl_2 was added in this solution. Then white precipitate (BaSO_4) was separated by the centrifuge and washed to the deionized water four times.

2.3. Determination of the sulfur



As shown as the equation, thiourea was easily transformed to urea by the oxidant, sodium bromate. Also sulfate ion and bromine were formed through the oxidation-reduction reaction, respectively. Then insoluble barium sulfate was precipitated with the addition of aqueous BaCl_2 in this solution.

Table 1 was shown the result of the reaction for thiourea and bromate ion. In the case of free thiourea (0 μL), the carrier (Na_2SO_4) was converted to barium sulfate of around 100% with an error tolerance ~1%. The oxidation of thiourea to sulfate needed at least 1.6 equivalent of bromate ion (Equation). Then thiourea was sufficiently oxidized by twice bromate ion (0.2 M NaBrO_3).

Table 1. The weigh of barium sulfate via weigh of thiourea in 1 mL (10 mg) of 7.04 mM Na₂SO₄ and acidic condition.

0.1 M Thiourea (μL)	0.2 M NaBrO ₃ (μL)	Cal. Weigh (mg)	Exp. Weigh (mg)	%Yield
0	0	16.4	16.2	99
10	10	16.6	16.3	98
20	20	16.9	16.3	96
30	30	17.1	17.2	99
50	50	17.6	17.3	98
70	70	18.1	17.9	99
100	100	18.8	19.0	101

On the basis of the sulfur oxidation of thiourea, thio-dATP (2'-deoxyadenosine 5'-O-(1-thio)triphosphate) could be transformed to sulfate and dATP, etc. And the change of the acidity and/or oxidant could be monitored.

3. Conclusion

The sulfur site of thiourea was oxidized to sulfate by using bromate ion as the oxidant in acidic solution (Equation). The oxidation of thiourea needed 1.6 equivalent of the oxidant (BrO₃⁻) with ~1% RSD. Then oxidized sulfate ion was quantitatively measured by the gravity method.

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