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Studies on Preparation of High Purity Sulfur. II. Removal of Trace Amounts of Selenium and Tellurium in Sulfur by Means of Distillation with Silver

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Synopsis. In the distillation without silver, most of the selenium and tellurium in crude sulfur appeared in the distillate. However, these impurities were removed by distillation using a column which was filled with silver and heated at 600—700 °C. The removal of them in the process was confirmed in a tracer experiment.

Selenium and tellurium are the main impurities in sulfur; however, few works have been published on the removal of trace amounts of these impurities.

Slepanov *et al.*[1] reported that 84.6% of the selenium in sulfur could be removed by treating molten sulfur in an aqueous magnesium chloride with nitric acid. Devyatykh *et al.*[2] reported that the removal of selenium was difficult during the purification of sulfur, by passing sulfur vapor through a high-temperature zone, because it formed a compound with sulfur. Nothing can be found in literature concerning the removal of tellurium in sulfur.

A method offers an investigation of distillation with silver as for the removal of selenium and tellurium in sulfur. A tracer experiment using ^{75}Se and ^{127m}Te has been undertaken in order to ascertain the effect of silver on the removal of trace amounts of the impurities.

Experimental

Determination of Selenium in Sulfur.[3] The sample solution was prepared by heating 5 g of sulfur with 15 ml of bromine and 60 ml of 30% nitric acid. To an aliquot of a sample solution (0.5 g sulfur), after neutralization, 12 g of ammonium chloride and 2 ml of 2 M formic acid were added and its pH was adjusted to 2—3. Ten ml of a 10% ethylenediaminetetraacetic acid solution and 2 ml of a 0.5% of diaminobenzidine solution were then added, the mixture was heated on a water both for 5 minutes and cooled, and its pH was adjusted to 6—7. The selenium complex in the solution was subsequently extracted in 10 ml of toluene, and its absorbance was measured at 420 nm.

Determination of Tellurium in Sulfur.[4] To an aliquot of a sample solution (1—4 g sulfur), about a 30 mg portion of ferric ions was added, precipitated with ammonia water, filtered, and washed with water. The solution obtained by dissolving the precipitate in 2 ml of 2 M hydrochloric acid and by then diluting the mixture to 10 ml with water was passed through an ion-exchange resin column (1 cm × 10 cm, Amberlite IR-120, H-form, 60 mesh). To the residue, obtained by evaporating the effluent and washing solution, 2.8 ml of water, 1 ml of a 40% ammonium citrate solution, and 2 ml of a 0.1% diethyldithiocarbamate solution were added, and the mixture was diluted to 10 ml with water. The tellurium complex in the solution was extracted in 5 ml of tributyl phosphate and measured at 400 nm.

Filling Material Containing Silver. The material, such as activated alumina, alumina ball, silica gel or a pumiceous substance, was digested in a silver nitrate solution. That containing silver was dried at 100 °C and then heated at 800 °C for 1 hr.

Preparation of Sulfur Containing ^{75}Se and ^{127m}Te. Into a flask of distillatory ^{75}Se (20 μCi, as Na_2SeO_3, 2.14 mCi/mg Se) and ^{127m}Te (450 μCi, as H_2TeO_3, 0.228 mCi/mg Te), 1 ml of hypophosphorous acid was added, and the mixture was dried at 100 °C. Into the flask a 30 g portion of sulfur was then taken, heated at 200 °C for 1 hr, and then distilled under a nitrogen atmosphere. The ^{75}Se and ^{127m}Te in the distilled sulfur were 41.5% and 92.6% respectively of these added to the flask.

Measurement of ^{75}Se and ^{127m}Te in Sulfur. In a 19-mmϕ aluminium dish, 0.5 g of sulfur was placed; then it was heated at 140 °C to melt and cooled slowly. The γ-rays from ^{75}Se and ^{127m}Te were simultaneously measured by the method described by Lee,[5] using a 100-channel scintillation spectrometer.

Distillation of Sulfur. The distilling apparatus used was the same as has been described in a previous paper.[6] The sulfur sample was distilled with a heated column, filled with filling material.

Results and Discussion

Table 1 shows the effect of silver on the removal of

TABLE 1. THE EFFECT OF SILVER FILLED IN COLUMN ON THE REMOVAL OF Se AND Te IN DISTILLATION OF SULFUR[a)]

Filling material[b)]				Distilled sulfur			Removal rate	
Silver (g)	Support (g)			Yield (%)	Se (ppm)	Te (ppm)	Se (%)	Te (%)
......	....	....	c)	98	117	46	10	18
Null	Pumiceous substance	(4—8 mesh)	20	98	117	26	10	54
Null	Activated alumina	(4—8 mesh)	42	98	117	30	10	46
12.6	Alumina ball[d)]	(2 mm ϕ)	81	96	75	17	42	70
4.2	Silica gel	(4—8 mesh)	40	96	87	12	33	79
8.6	Activated alumina	(4—8 mesh)	42	94	2.5	0.9	98	98
9.0	Pumiceous substance	(5—8 mm grain)	20	94	4.8	3.3	96	94

a) Sulfur sample: Amount; 10 g, Se content; 130 ppm, Te content; 56 ppm. Column temperature: 600 °C. b) The bed of filling material was about 20 cm long. c) Distillation without filling material. d) Commercial support for catalyst.

TABLE 2. THE RESULT OF TRACER EXPERIMENT ON DISTILLATION OF SULFUR CONTAINING ^{75}Se AND ^{127m}Te[a]

Filling material[b]		Distilled sulfur					Removal rate	
Silver (g)	Support (g)	Yield (%)	Se total activity (cpm)	Te total activity (cpm)	Se (ppm)	Te (ppm)	Se (%)	Te (%)
	c)	99	265685	42276	2.71	5.57	9.7	11.6
	c)	99	286198	45886	2.92	6.04	2.7	4.1
Null	Pumiceous substance 3	97	272309	37121	2.78	4.89	7.4	22.4
Null	Activated alumina 5	97	271639	29777	2.77	3.92	7.6	37.8
0.85	Pumiceous substance 3	96	2472	790	0.025	0.104	99.2	98.4
0.85	Activated alumina 5	96	2261	408	0.023	0.063	99.2	99.0

a) Sulfur sample: Amount; 2 g, Se content; 3.00 ppm, Te content; 6.30 ppm, Se total activity; 293959 cpm, Te total activity; 47839 cpm. Column temperature: 600 °C. The bed of filling material was about 7 cm long. b) 8—12 mesh. c) Distillation without filling material.

selenium and tellurium. In the distillation without silver, most of the selenium and tellurium in crude sulfur appeared in the distillate. However, both the impurities were removed by distillation using a column filled with silver supported on a pumiceous substance or activated alumina. The effect of silver is related to the affinity of silver for selenium and tellurium. It has been established that silver has more affinity for selenium than for sulfur.[7] It seemes that silver reacts slowly with sulfur, but reacts rapidly with selenium and tellurium in the process. Consequently, sulfur passed through the column, while selenium and tellurium remained in the column.

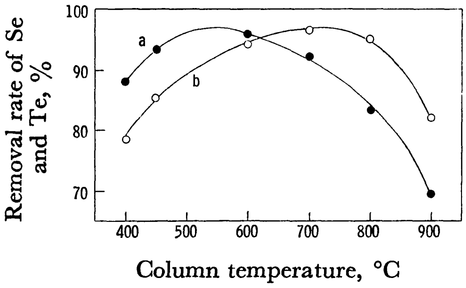

Fig. 1. The effect of temperature of column filled with silver on the removal of Se (a) and Te (b).
Sulfur sample: Amount; 10 g, Se content; 117 ppm, Te content; 56 ppm. The column was filled with 2 g of silver supported on 20 g of pumiceous substance (4—8 mesh) about 20 cm long.

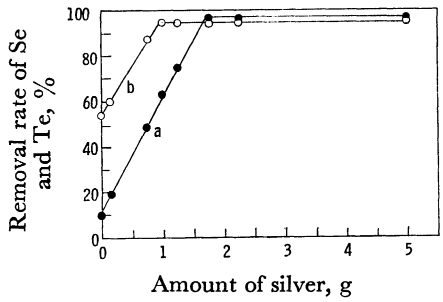

Fig. 2. The effect of amount of silver in column on the removal of Se (a) and Te (b).
Sulfur sample: Amount; 10 g, Se content; 117 ppm, Te content; 56 ppm. The columns were filled with various amounts of silver supported on 20 g of pumiceous substance (4—8 mesh) about 20 cm long. Column temperature: 600 °C.

Figure 1 shows the effect of the column temperature on the removal of the impurities. Both impurities were effectively removed with the column heated at 600—700 °C.

Figure 2 shows the effect of the amount of silver in the column on the removal of the impurities during the distillation of 10 g of sulfur. Effective removals of selenium and tellurium were shown when more than 1.7 and 1.0 g of silver respectively were present in the column. The reduction of the amount of silver in the column caused a decrease in the removal rates of the impurities; this was because the sulfuration of silver in the column progressed rapidly, while produced sulfide did not react with selenium and tellurium.

The reproduction of the column in which silver had been converted into sulfide was easily carried out by passing air or oxygen through the column heated at more than 600 °C.

The removal of them was confirmed in a tracer experiment as shown in Table 2.

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