

Kiba reagent method of sulfur extraction applied to isotopic work

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Abstract

Tin(II)-strong phosphoric acid("Kiba reagent") is an excellent chemical reagent that can extract, in the form of hydrogen sulfide, even trace amounts of sulfur from various materials. It is extremely powerful in processing pyrite and is quite suitable in recovering, for isotopic study, the low concentrations of sulfur in most rocks.

Introduction

Tin (II)-strong phosphoric acid (to be called "Kiba reagent" hereafter) was first described by KIBA *et al.* (1955) as a powerful reducing reagent taking sulfate to hydrogen sulfide. It has been successfully applied to the rapid quantitative analysis of various forms of sulfur, both organic and inorganic (KIBA and KISHI, 1957; KIBA *et al.*, 1957 a, b; OHASHI, 1955) and to the determination of minor amounts of sulfur in some igneous rocks (ARIKAWA *et al.*, 1972). More recently we have recognized that the reagent is very useful in sulfur isotopic work for its remarkable efficiency in extracting sulfur from diverse sulfur-bearing materials with a very simple procedure (SASAKI *et al.*, 1976). Isotopic study of rock sulfur for which we have very limited data to date can thus be made routinely and there are indications that such studies will provide us valuable information related to petrogenesis, as exemplified by recent work on granitoid sulfur by SASAKI and ISHIHARA (1979). Considering its potential importance to sulfur isotope workers, we here sum up the "Kiba reagent" method of sulfur extraction, following the original description by KIBA *et al.* (1955) with a few minor modifications.

Preparation of Kiba Reagent

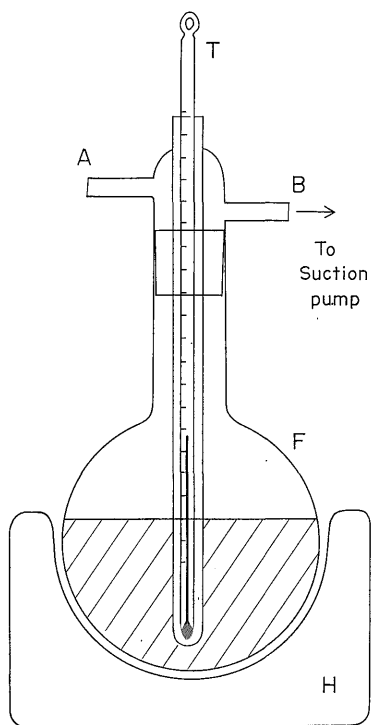
The Kiba reagent used in our laboratory is prepared as follows. Take 300 ml of ortho-phosphoric acid of extra pure grade ($d=1.7$) in a 500 ml pyrex glass flask, and dehydrate it by heating to 250°C for an hour. Evolved vapour in this heating should be removed immediately through a suction pump as described in Fig. 1. Using a mantle heater is recommended to avoid a possible hazardous gush of the acid.

After cooling to 150°C, add 30 to 40 g of tin (II)-chloride dihydrate of extra pure grade to this strong phosphoric acid. Heat the whole mixture up to 280°C, again within an hour, but this time under a current of nitrogen gas which flows through A to B in Fig. 1. Hydrogen chloride evolved from the reacting mixture is carried away with the nitrogen stream

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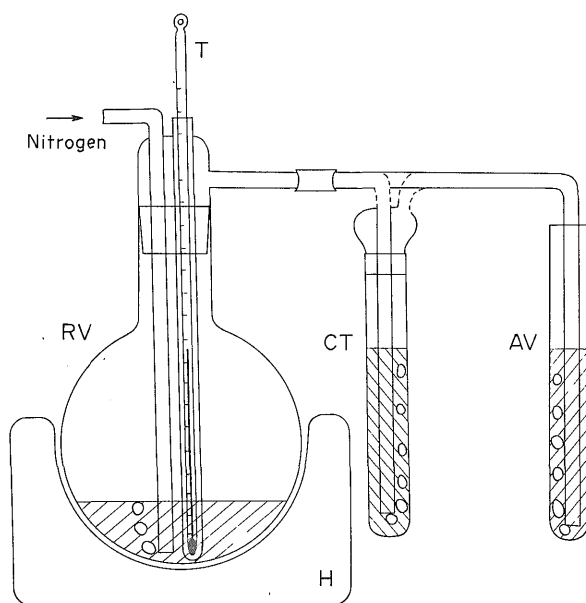
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F: 500 ml pyrex glass flask
T: Thermometer (360°C)
H: Mantle heater

Fig. 1 Apparatus for preparation of Kiba reagent.



RV: Reaction vessel (300 ml pyrex glass flask)
AV: Absorbing vessel
CT: Chlorine trap
T: Thermometer
H: Mantle heater

Fig. 2 Apparatus for sulfur extraction.

and all sulfur-bearing impurities which might have been contained in the chemicals will be removed as hydrogen sulfide as well. Keep nitrogen gas flowing through the apparatus till the reagent cools down below 150°C.

Amounts of stannous ion in the reagent can be changed depending upon the amount of sulfur to be reduced in specimen. Thus, for rock specimens with low concentrations of sulfur, the reagent may be prepared with lesser amounts of tin (II)-chloride dihydrate.

Sulfur Extraction Procedure

Processing of samples may be carried out with a flask similar to that described in Fig. 1, using nitrogen gas from a cylinder as the carrier for the evolved hydrogen sulfide. However, to get the sample-reagent mixture more thoroughly agitated, the reaction vessel illustrated in Fig. 2 may be more appropriate. Evolved hydrogen sulfide is simply bubbled through zinc acetate solution to fix the sulfur as zinc sulfide. The zinc acetate solution is prepared by dissolving 40 g of zinc acetate dihydrate of pure grade in 100 ml distilled water, then adding 30 ml of glacial acetic acid and finally diluting to 1000 ml with distilled water.

Only a small amount of the reagent is enough to reduce fairly large amounts of sulfide

or sulfate to hydrogen sulfide; some 50 mg of pyrite or barite can be treated by less than 20 ml reagent. For extraction of common rock sulfur, 10 ml reagent for 1 to 1.5 g of sample may be an appropriate ratio.

After placing the sample and Kiba reagent in the reaction vessel and connecting it to the absorbing vessel (Fig. 2), nitrogen gas is allowed to flow through the whole setup for a few minutes at a rate of some 200 bubbles per minute. Then the reaction vessel is heated up to 280°C in about 15 minutes under the same rate of nitrogen stream. When rock samples are treated, a trap filled with distilled water is useful between the reaction and absorbing vessels to avoid possible contamination of the absorbing solution by chlorine.

Evolution of hydrogen sulfide starts at varying temperatures above 120°C depending upon the specimen. However, the reaction goes very quickly, and is usually completed before the temperature reaches 280°C. An additional 10 to 15 minutes processing at $280^{\circ} \pm 10^{\circ}\text{C}$ is recommended, particularly for rock samples, to ensure completion of reaction. By this time rock-forming silicates will be thoroughly decomposed releasing any sulfur that might have been included.

Zinc sulfide precipitate is converted to silver sulfide by adding 0.1 N silver nitrate solution. The mixture is then simply boiled for about one minute, so that the silver sulfide coagulates coarsely enough to be easily filtered over glass wool.

Dense viscous residue which may adhere to the vessel wall as it cools can be washed out by hot water or by boiling the sticky residue with water.

Results and Conclusions

Quantitative recovery of sulfur from sulfide and sulfate minerals by Kiba reagent was established by KIBA *et al.* (1955; 1957 a). This broad spectrum in efficacy as well as simplicity and rapidity of the technique is outstanding. It is of particularly importance that the reagent can extract pyrite-sulfur so easily, a mineral which otherwise has to be treated by more troublesome processes including oxidation with acids, evaporation, re-solution, filtration etc. Since pyrite is the most common sulfur carrier in many kinds of rocks, the isotopic study of rock sulfur can be practiced routinely by the use of Kiba reagent.

Some workers have been using the so-called Thode solution (a mixture of HI, HCl and H_3PO_2 used by THODE *et al.*, 1961 for reduction of sulfate) to recover the whole rock sulfur (e. g. SCHNEIDER, 1970). However, this reagent reacts with pyrite only very slowly and quantitative extraction of sulfur is barely accomplished even after several tens of hours processing. Besides, silicates are not decomposed by Thode solution and fine-grained inclusions of sulfur-bearing material in silicates may have no chance to react with the solution.

In Table 1 we compare the results of sulfur extraction from pyrite-bearing rocks using the two reagents. The efficiency of Kiba reagent will clearly be noticed. It follows that pyrite-sulfur may be separated chemically from coexisting sulfates by using the two reagents: Thode solution first for sulfates and Kiba reagent for pyrite in the residue. Some such examples are shown in Table 2. However, when the specimen contains other forms of sulfide such as galena, sphalerite, pyrrhotite and chalcopyrite, for instance, this method of sulfide-sulfate separation is of course not applicable. Recently, SAKAI *et al.* (1978) reported that the Kiba reagent method performed under vacuum can separate any form of

Table 1 Comparison of efficiency of sulfur extraction from pyrite-bearing rocks by Kiba-reagent and Thode-solution.

Sample and locality	Amounts of sample	Reagent used	Amounts of reagent	Time of reaction	Sulfur analysis
Hornblende-biotite granodiorite, Susaka, Nagano Pref.	1.001 g	Kiba	10 ml	40 min	0.97%
	0.564	Kiba	10	20	0.96
	1.012	Thode	40	120	0.07
Amphibole quartz gabbro, Zakka, Shimane Pref.	3.006	Kiba	30	45	0.10
	4.202	Kiba	30	30	0.10
	4.020	Thode	40	120	0.007

Table 2 Fractional separation between sulfate-sulfur and pyrite-sulfur by means of successive reaction with Thode solution and Kiba reagent.

Sample	S(%)			$\delta^{34}\text{S}(\text{‰})$		
	W.R.	Sulfate	Sulfide (py)	W.R.	Sulfate	Sulfide (py)
Rhyolite, Kosaka mine, Akita Pref.	0.62	0.18	0.44*	-1.7 -1.5*	+0.2	-2.2
Tonalite boulder, diatrene, Con mine, Yellowknife, Canada	1.045	0.032	1.013*	-3.5 -3.8*	+7.0	-4.1

* Calculated

sulfide from sulfates.

Although the efficiency of Kiba reagent as a sulfur extractor is remarkable, it is not omnipotent and there exist a few common sulfides hardly or only partially attacked by the reagent. They include Cu-bearing sulfides, arsenopyrite and molybdenite. Elementary sulfur is also difficult to process with this technique. Chalcopyrite, the most common copper-bearing sulfide, releases some 75% of sulfur after normal processing procedure, while the remainder forms chalcocite (Cu_2S) in the solution which seems to resist further decomposition. A small kinetic isotope effect would be inevitable in such a partial extraction, though it may be negligible unless the mineral carries the major part of the sulfur in the specimen. In any case, however, ore-microscopic examination is essential for any rock specimen under investigation.

Acknowledgement

The work was initiated at the University of Alberta where the senior author stayed for three months in 1975. Financial support from the National Research Council of Canada is gratefully acknowledged.

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木羽試薬によるイオウ同位体研究試料の調製法

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要 旨

スズ強リン酸(木羽試薬)は各種試料からのイオウ抽出剤として、イオウ同位体研究に、きわめて広い適用範囲を持っている。とくにこれまで適当な処理方法が見当たらないために、ほとんど手がつけられていなかった岩石中の微量イオウの同位体的研究は、本試薬の使用によって、はじめて簡便迅速に行いうるようになった。その方法につき記載し、2, 3の問題点を論じた。

(受付: 1978年10月25日; 受理: 1978年12月11日)