Titrimetric analysis for silicon

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SUMMARY. Rapid, accurate silica determinations have been made titrimetrically following decomposition by $HClO_4$–HF in a 'Teflon' vessel, the volatilized silicon tetrafluoride being precipitated as K_2SiF_6 in a HF–KF–glycerol–alcohol mixture. After filtration and washing with alcohol the precipitate is dissolved in boiling water, then titrated with NaOH. This method has many advantages over conventional gravimetric or spectrophotometric procedures.

THE classical gravimetric determination of silica (Washington, 1930; Hillebrand, 1953) although comparatively accurate, is time consuming and not without problems in the analysis of certain samples of unusual composition. For most rocks and minerals, it is necessary to recover the small amount of silica that passes into the ammonia (R_2O_3) precipitate (Smales and Wager, 1960). The ignition and subsequent pyrosulphate fusion is also tedious and furthermore it is not a logical step in recently developed analytical procedures (cf. Shapiro and Brannock, 1956). On the other hand, 'rapid' spectrophotometric or atomic absorption methods (Langmyhr and Graff, 1965; Katz, 1968), subject to limitations of instrumental precision, are not adaptable to quantitative analysis of materials in which SiO_2 is the major component.

Utilization of the volatility of SiF_4 from silicate samples decomposed by hydrofluoric acid has so far been limited by the difficulty of obtaining closed containers (Story-Maskelyne, 1870) resistant to attack by HF but with the development of polytetra-fluoro-ethylene ('Teflon') this problem no long exists. This article describes a method of determining silica titrimetrically; silica is distilled as fluosilicic acid (H_2SiF_6), which reacts with potassium fluoride (KF) to form a heavy precipitate of potassium silicofluoride (K_2SiF_6), and this precipitate is titrated with alkali: $K_2SiF_6 + 4NaOH \rightarrow 2KF + 4NaF + H_4SiO_4$. This method, which has been successfully tested on a range of rock and mineral samples, is rapid and allows high precision irrespective of the abundance of silica in the analysed sample.

The *apparatus* necessary for the determination of silica titrimetrically are a decomposition vessel, a recovery vessel, a filter assembly, and a stand.

The decomposition vessel consists essentially of two parts, each of which may be moulded or manufactured from block or rod 'Teflon' on a simple metal-working lathe. The decomposition vessel may also be made from brass or another appropriate metal with the inner surfaces coated with 'Teflon' or with platinum. The lower heating chamber (A, fig. 1) screws into the upper delivery–extraction block (C, fig. 1), complete sealing of the assembled vessel being ensured by a small 'Teflon' washer (B, fig. 1). Two holes are drilled from one end of the delivery–extraction block to a cavity above the female screw fitting at the other end. A piece of 'Teflon' rod $\frac{1}{8}''$ in diameter

and $\frac{7}{16}''$ in length is used to block the horizontal hole $\frac{1}{8}''$ in diameter at the recovery vessel end of the delivery–extraction block; this hole is the channel through which HF is delivered to the heating chamber. It may be connected by polythene tubing to a separate 'Teflon' stopcock and acid container, or as shown in fig. 1 the stopcock (D) may be incorporated in the block itself and the HF added from a plastic syringe.
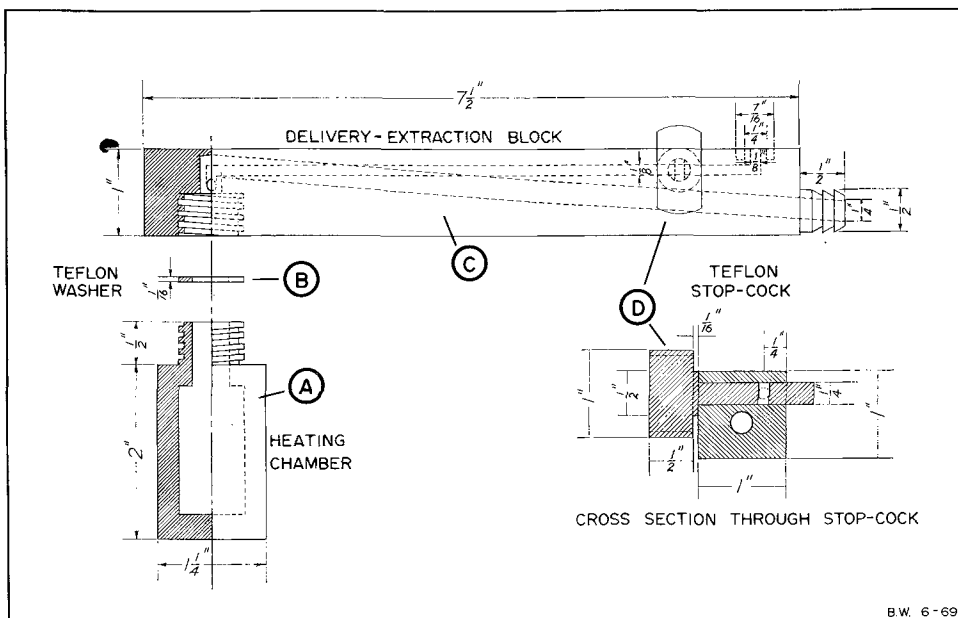

FIG. 1. 'Teflon' decomposition vessel for distillation of silicon as H_2SiF_6.

Volatilized SiF_4 (or condensed H_2SiF_6) passes through the inclined channel, which is shaped to take a polythene tube that passes into the recovery vessel. The delivery–extraction block must be long enough to prevent overheating of the polythene tube connections.

The recovery vessel is a polythene container of $c.$ 120 ml capacity (A, fig. 2), preferably having sloping sides and a stopcock fitted to the base. In practice it has been found that containers of the type in which standard volume reagents are supplied (e.g. M & B 'Volucon'), if cut away at the upper end, suit the purpose ideally, a tube and clamp being used to replace the stopcock. The container may be graduated in approximately 5 ml divisions. A tapered polythene rod hollow at one end (see B, fig. 2) is inserted into the neck of the recovery vessel and assists the subsequent filtration process by holding back the majority of the precipitate (K_2SiF_6) while most of the mother liquid is drained off onto the filter.

The filter assembly consists of a 2 in. polythene funnel attached to a polythene Buchner flask. Suction apparatus should be arranged so that HF fumes are expelled into a fume cupboard. Whatman 540 or 542 filter paper has been found most suitable.

A suitable stand, preferably one incorporating a reflector to prevent overheating

of the recovery vessel, is used to hold the assembled apparatus. Up to ten sets of apparatus may be operated simultaneously.

Analytical procedure. Before assembling the decomposition vessel 1 ml of conc. $HClO_4$ is added to the accurately weighed 1 gm sample in the heating chamber. Positioned on the hot plate the decomposition vessel is connected to the recovery vessel containing 55 ml of the recovery mixture, which is prepared by dissolving 2 gm KF in 15 ml HF, then adding 20 ml of glycerol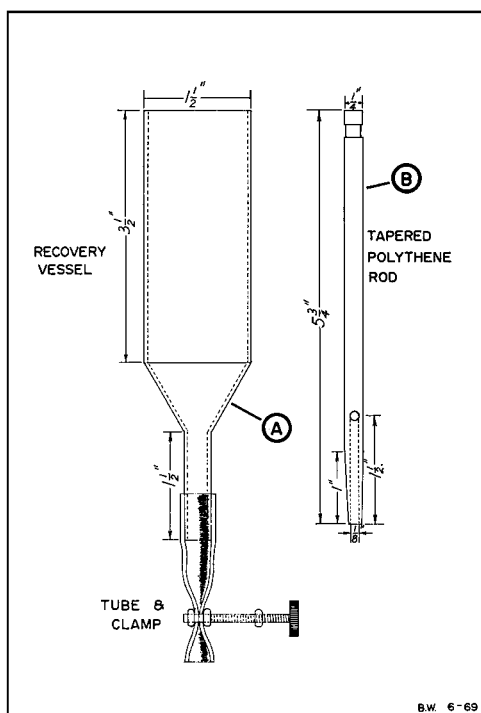 and 20 ml of ethyl alcohol with continuous stirring. If a precipitate forms during preparation HF is added to the recovery mixture until the precipitate dissolves. The recovery mixture may be prepared in bulk and stored. It is essential that the polythene tube delivering the volatile SiF_4 (or condensed H_2SiF_6) to the recovery vessel extend as close as possible to the bottom of the latter. To the heating chamber via the upper channel in the delivery–extraction block 10 ml of HF is delivered. The stopcock is closed immediately and the delivery tube or syringe is removed. With the hot plate set at 220 °C the decomposition vessel is heated until perchloric acid fumes are evolved (approx. 90 min). To obtain a better distribution of heat the upper portion of the decomposition vessel is heated by an infra-red lamp. After considerable heating the vapour pressure in the decomposition chamber falls to such an extent that significant back suction from the recovery vessel is developed. This back suction is eliminated by simultaneously opening the acid delivery stopcock and gently blowing through a long plastic tube (*c.* 3 ft) attached to the acid delivery stopcock. Heating is continued and when back suction develops a second time the blowing process is repeated for about 30 sec. Continue heating until no more $HClO_4$ fumes escape.

FIG. 2. A. Polythene recovery vessel. B. Polythene rod, used to assist subsequent filtration.

With the acid delivery stopcock left open the decomposition vessel is cooled by removing from the hot plate for 30 min. Unscrew the heating chamber from the delivery–extraction block and proceed to wash with alcohol both channels in the delivery–extraction block, including the stopcock and the connecting tube into the recovery vessel. Allow 30 min for the K_2SiF_6 precipitate to settle in the recovery vessel before filtering.

Placing the recovery vessel over the filter assembly open the stopcock or clamp. The tapered rod that fits into the neck of the recovery vessel holds back the bulk of the K_2SiF_6 precipitate while most of the mother liquid is drained off onto the filter. With the suction pump operating the tapered rod is raised allowing the bulk of the precipitate to pass onto the filter. The tapered rod and the recovery vessel are washed with 6 to 8 10 ml portions of alcohol and the edge of the filter paper with 3 or 4 20 ml portions of alcohol. The filter paper and the precipitate are dried in an oven at 80 °C for 15 minutes before being plunged into 500 ml of boiling water and simmered with continuous stirring for 5 minutes, by which time all the precipitate should be dissolved. Bromo-thymol blue is used as an indicator, 1 ml of a 0·1 % solution, but phenolpthalein should be used instead if carbon is present in the sample and a correction factor is then necessary (determine with a standard sample using a pH meter; the equivalent point is pH 7·1).

The hot solution is titrated with 0·5 N NaOH and if the yellow-blue end point is missed, back titrate with 0·5 N HCl. 0·1 ml of 0·5 N NaOH is equivalent to 0·75 mg SiO_2.

In order to obtain accurate silica determinations it is absolutely essential that the following precautions are heeded:

Not less than 10 ml HF (40 %) should be added to the decomposition vessel and heating must proceed until white fumes of perchloric acid cease to evolve, at this stage the residue in the heating chamber is virtually dry.

The decomposition vessel must be well sealed. A satisfactory test is, after assembly of the vessel, to blow into the polythene tube that will be placed into the recovery vessel, and to test for the retention of pressure. However, since leaks developed during decomposition constitute the main source of possible error, duplicate analyses should be performed wherever possible. Leakages only develop in apparatus made entirely of 'Teflon' as these apparatus undergo deformation after prolonged use.

The amount of KF added to the recovery mixture must be sufficient to convert all SiF_4 to K_2SiF_6, and to allow an excess necessary to reduce the solubility of K_2SiF_6 in the glycerol–alcohol recovery mixture. It is important, however, to ensure that all excess KF remains dissolved in the recovery mixture plus washings, for any that is precipitated tends to absorb HF and will consequently affect the subsequent titration. Experiments on various samples have shown that the recovery mixture prescribed above gives satisfactory results from 0 to 1·0 gm SiO_2.

Results. The above method has been successfully tested on and is now employed routinely in analyses of rocks, minerals, soils, and ores. In sulphide-bearing and manganiferous samples it avoids problems connected with attack on platinum-ware, and the general advantages include saving of time (10 determinations take approximately 5 hours) and comparatively low cost (10 sets of the 'Teflon' apparatus are equivalent in expense to one set of conventional platinium-ware). When combined with atomic absorption and other modern techniques, a relatively accurate complete analysis may be undertaken on small quantities, a considerable advantage when working on mineral concentrates where frequently 0·5 gm or less of material is

available. As an illustration of the accuracy and precision of the method, results are listed in table I for several standard rock samples and for differing sample weights of 'specpure' silica glass.

TABLE I. *Results for standard samples*

GI		WI		DTSI		Argillaceous limestone No. 1A		Herosil	
Weight used	SiO$_2$ found	Weight used	SiO$_2$ found	Weight used	SiO$_2$ found	Weight used	SiO$_2$ found	Weight used	SiO$_2$ found
1·0013 g	72·58 %	1·0004 g	52·55 %	1·0000	40·51 %	1·0009 g	14·10 %	0·4000 g	100·02 %
0·5008	72·55	0·5011	52·54	0·5005	40·47	0·5002	14·07	0·1000	99·93
0·2516	72·52	0·2507	52·54	0·2510	40·42	0·2508	14·03		
Accepted value	72·50		52·60		40·45		14·11		100·00
Reference:	Stevens and Niles, 1960		Stevens and Niles, 1960		Flanagan, 1969	U.S. Dept. of Commerce, Bureau of Standards, 1931			

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