AN IMPROVED METHOD OF SILICON-32 MEASUREMENT OF GROUNDWATERS

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ABSTRACT

A rapid method of separation of ^{32}P from ^{32}Si by hydrofluorisation saves considerable amount of time besides being more efficient in the chemical recovery of phosphorus. Similarly, 4π beta counting of ^{32}P activity allows a more accurate estimation of small amounts of this activity. These improvements make it possible to reliably measure amounts of ^{32}Si as low as 0·1 dpm present in about 10 tons of water.

INTRODUCTION

THE usefulness of cosmic ray produced silicon-32 for studying the gound-water movements has been realized during the past decade[1]. Recent measurements have all shown that its half life centers around 350 ± 50 years[2–4] which makes ^{32}Si particularly suitable for dating groundwaters up to about 1500 years. The activity levels of this radionuclide were measured in natural waters and are found to be in the range of 0·01–0·5 dis/min per metric ton of water[5, 6]. The groundwaters, like surface ocean waters[7], have very low ^{32}Si concentrations. For this reason, about 5–20 tons of groundwater is usually processed at the site of collection for Si recovery, and subsequent purifications, etc., are carried out in the laboratory[8]. Usually, 100–300 g of pure SiO_2 is recovered from each groundwater sample which is stored for a period of about two months to allow the growth of ^{32}P (E_{max} $\beta^- = 1{\cdot}7$ MeV) into secular equilibrium with its parent ^{32}Si. The ^{32}P is then separated from its parent and assayed for its beta activity. The chemical procedures adopted earlier were time consuming besides being less efficient. Also the ^{32}P counting was done using 2π geometry beta counters, which can be replaced by doubly-efficient 4π systems. In this paper, we describe two technological developments by which the chemistry is done more rapidly and efficiently and the beta activity of ^{32}P is assayed with a factor of two better efficiency compared to the earlier method.

EXPERIMENTAL TECHNIQUES

The extraction and purification of SiO_2 from groundwaters and the assay of ^{32}Si is described in detail by Nijampurkar[9]. Here we describe the two improvements that have been introduced recently.

1. *Separation of ^{32}P from ^{32}Si*

The technique essentially involves the distillation of Si as SiF_4 at 110° C and the absorption of SiF_4 vapours in pure water leaving behind phosphorus (^{32}P) in the distillation flask.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6$$

The experimental set-up is shown in figure 1. The distillation flask is made out of pure silver which can take upto 250 g . SiO_2. SiF_4 is absorbed in PVC absorbers F_1 and F_2, each containing 7 liters of double-distilled water. Absorber F_3, containing 5 liters of 4*M* NaOH, removes traces of HF, if any. The last bottle F_4 is left empty to prevent liquids from getting carried into the rotary pump used for suction.

Purified SiO_2 (in which ^{32}P is in equilibrium with ^{32}Si) is placed in the silver flask. Stoichiometric amount of HF needed to convert it to SIF_4 *plus* a 10% excess is added to the flask. Stable phosphorous carrier (equivalent to 40 mg $Mg_2P_2O_7$) in the form of Na_2HPO_4 is also added and the

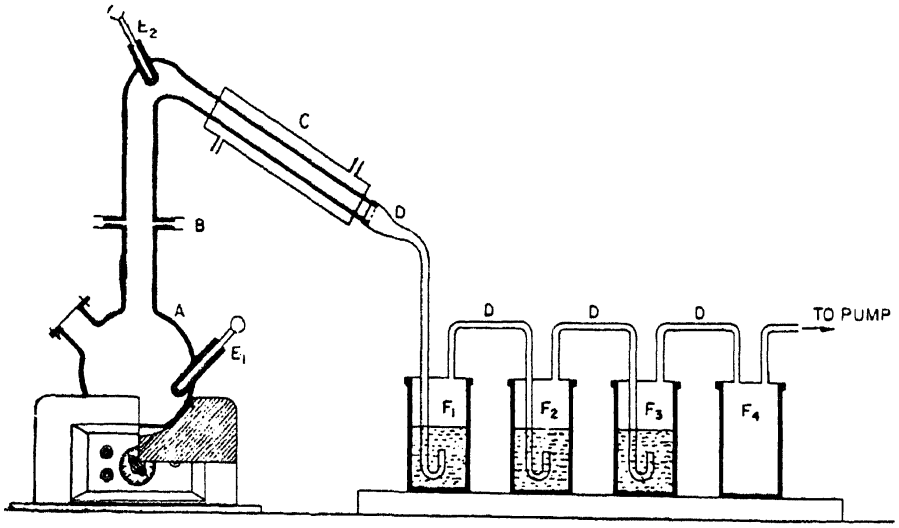

Figure 1. Si distillation apparatus. A, B, Long-neck silver flask; C, Water-Condenser; D, PVC tubes; E_1, E_2, Thermometers; F_1, F_2, Water Absorbers for SiF_4; F_3, Alkali Absorber; F_4, Empty Flask.

setup is arranged as shown in figure 1. The silver flask is heated electrically. The temperature raises to 110° C and remains constant until all the Si is distilled as SiF_4. It usually takes about 8 hr to distil 250 g SiO_2. The hot SiF_4 vapours are cooled during passage through a water condenser C (*see* figure 1) and get absorbed almost quantitatively in absorber F_1. A rise in temperature is indicative of the completion of the reaction.

About 100 ml of 2·5 *M* HCl is added to the silver flask to dissolve the 'P', the solution is filtered, dried and the residue redissolved in 4*M* HNO_3. Phosphorus is precipitated as ammonium phosphomolybdate and is purified according to the procedures described by Kharkar *et al.*[8]. The chemical yields with this procedure are almost quantitative, compared to 50–90% (average about 70%) using the earlier procedure (figure 2).

2. *Silica recovery*

As mentioned earlier, most of the SiF_4 vapours are absorbed in F_1 (figure 1), the first water-absorber. The second absorber as well as the NaOH absorber (F_3) have negligible amounts of SiO_2. Silica can be

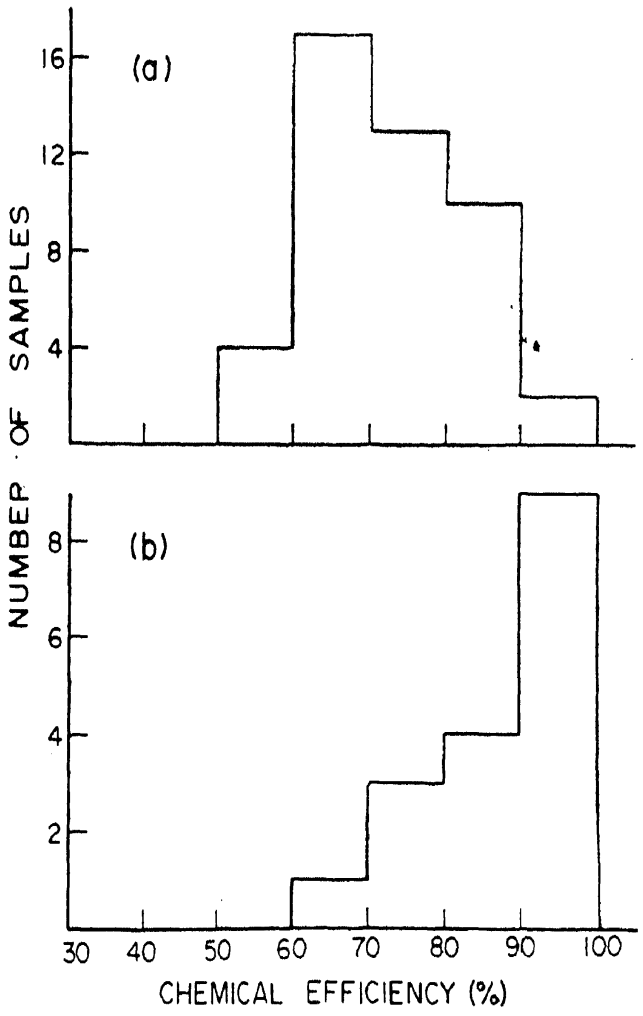

Figure 2. Histogram of chemical efficiency *versus* number of samples. (*a*) using the earlier method, (*b*) with the improved method.

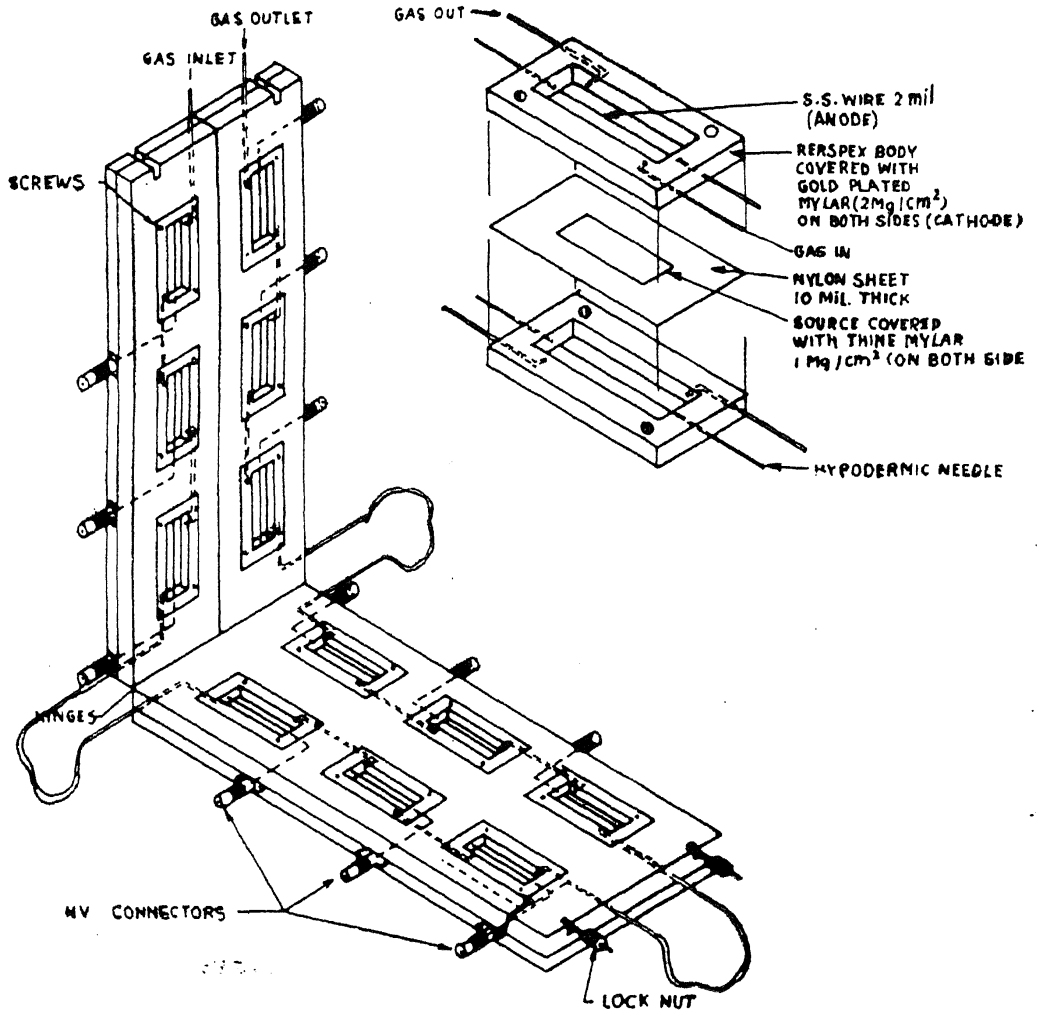

Figure 3. Schematic view of the six 4π beta systems in the open position. Six pairs of counters can be seen.

precipitated from water in absorbers F_1 and F_2 with either NH_4OH or NaOH as follows:

$$H_2SiF_6 + 6NH_4OH = 6NH_4F + 4H_2O + SiO_2$$

$$H_2SiF_6 + 6NaOH = 6NaF + 4H_2O + SiO_2$$

In the case of NH_4OH the hydrous-silica-precipitate is filtered, washed with distilled water and ignited at 850° C to SiO_2. With NaOH, part of the silica remains in solution and so the NaOH solution is acidified with HCl and taken to dryness. The dried material is then dissolved in water and filtered. The precipitate (hydrous silica) is washed, dried and ignited to anhydrous SiO_2. The NH_4OH method is simple, but the SiO_2 recovery is only 60–75%. Attempts are currently under way to increase the silica recovery.

3. 4π *beta counting of* ^{32}P *activity*

With the aim of improving the sensitivity of the counting systems[11], a twin-2 π beta system, resembling a 4π system, has been developed[12]. The source is sandwiched between two 2π type beta counters. The background of the system is kept low by demanding that none of the signal pulses from either of the 2π beta-counters be in coincidence. In addition, the conventional anticoincidence umbrella for eliminating pulses due to cosmic ray particles, mainly muons, is used[12].

Constructional Details.—The source to be counted is sandwiched between two identical flow-gas type Geiger counters, size 5 cm × 3 cm × 0·5 cm with an active area of 3·3 cm^2. For allowing continuous counting of several samples for over periods of two to three half-lives of ^{32}P (*i.e.*, 4–6 weeks), six identical 4π beta systems have been built (figure 3)[12]. These systems are operated inside 40 cm × 25 cm × 60 cm metallic shield of 10 cm thickness (5 cm of pure lead followed by 5 cm of steel outside). The entire six-counter system is placed directly over a rectangular guard counter (flow-gas type) of dimensions 45 cm × 27·5 cm. The area of the guard counter is large enough to cover a 2π solid angle so that most of the muons get cancelled. The background of the counter is further reduced by placing a 6 mm thick, pure lead sheet over them. Phosphorus extract (chemical form

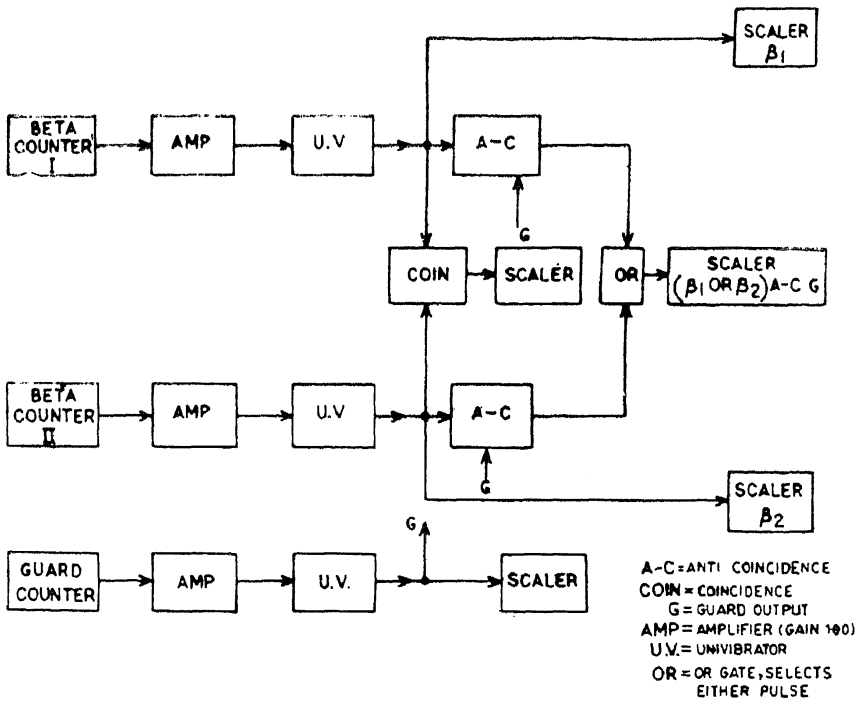

Figure 4. Block diagram of the electronics for the 4π beta counting system.

Table 1. *Characteristics of the 2 π and 4 π beta counting systems*

Characteristic	2 π system		4 π system		
	1	2	1	2	3
Background (counts per hour)	1·6	1·9	3·9	4·5	3·9
Counting efficiency (%) for 40K betas	35	38	67	72	71
Figure of merit (S^2/B)	750	755	1150	1150	1300

$Mg_2P_2O_7$) from each sample is made as a sandwich between two 0·9 mg cm^{-2} thick mylar films on an area of 1·68 cm^2 in the rectangular slit of 2·4 × 0·7 cm cutout in a 250 mil thick nylon sheet.

4. *Electronics for the 4 π beta system*

A block diagram of the electronic system is shown in figure 4. A dc-dc converter supplies the high voltage to the counters. The signal pulse is monitored through an exclusive OR gate—*i.e.*, any pulse counted is that which occurs solely in either of the beta counters with no simultaneous pulse from either the ' other ' beta counter (OR-mode), or the guard counter (A–C mode). This was done since any ^{32}P beta radiation that emerges out of the source will produce only one pulse in either of the beta counters. The part of the background which is constituted by coincident pulses, for instance, due to the Compton electrons arising in any one of the counters and reaching the other, is eliminated.

5. *Performance data of 4 π beta systems*

In table 1, we have given the performance data of three of the six 4 π systems. For the sake of comparison, the data of two of the 2 π systems which have been used in this work are also given. As expected, the figure of merit of the 4 π systems is superior to those of the 2 π and compares favourably with other counting systems developed in recent years[13–15]. The backgrounds of all the counting systems (table 1) are stable over long periods of time (six months).

Table 2. *Relevant details of surface and groundwater samples*

Sample	Location (Latitude, Longitude)	Depth (m)	Weight of SiO_2 milked (g)	Equivalent volume of water (metric tons)
Bhairwa Tube Well (1st Aquifer)	W. Rajasthan (26° 55′ N, 71° 17′ E)	73 to 127	180 150	(*a*) 11·5 (*b*) 9·6
Bhairwa Tube Well 2nd Aquifer)	do.	135 to 165	240 145	(*a*) 14·1 (*b*) 8·5
Devikot Tube Well	W. Rajasthan (26°41′ N, 71°10′ E)	132	165 103	(*a*) 9·8 (*b*) 6·1
Neran Dug Well	W. Rajasthan (26° 48′ N, 71° 28′ E)	38 to 43	262 193	(*a*) 8·1 (*b*) 6·1
Ganges River Water	Hardwar Uttar Pradesh (30° N, 78° E)	—	70 68	(*a*) 8·3 (*b*) 8·2
Pilvai Tube Well	Gujarat (23° 25′ N,72° 47′ E)	140	149 132	(*a*) 4·4 (*b*) 3·9
Mulund Tube Well	Maharashtra (19° N, 73° E)	33	240 70	(*a*) 6·6 (*b*) 1·9
Shankarapura Tube well	Uttar Pradesh	60	197 175	(*a*) 6·1 (*b*) 5·5

a and *b* denote first and second milking respectively.

Results and Discussion

Each sample is counted continuously in a 4π counter for 4–6 weeks, the gross counting rates are ascertained approximately every 24 hr. In the case of 2π counting, the samples are counted at regular intervals (a few days each time) in the same counter for about 6–8 weeks. In all cases, the gross

Table 3. *^{32}Si concentration in surface and groundwaters*

Sample		Precipitation method				Hydrofluorisation method			
		2 π-counting		4 π-counting		2 π-counting		4 π-counting	
		Net ^{32}P cph	^{32}Si dpm/10^3 L	Net ^{32}P cph	^{32}Si dpm/10^3 L	Net ^{32}P cph	^{32}Si dpm/10^3 L	Net ^{32}P cph	^{32}Si dpm/10^3 L
Bhairwa Tube Well (1st Aquifer)	(*a*)	..	..	..	..	2·2	0·01±0·005	..	..
	(*b*)	..	..	..	..	1·8	0·014±0·003	..	..
Bhairwa Tube Well (2nd Aquifer)	(*a*)	..	..	..	..	..	..	6·2	0·012±0·003
	(*b*)	..	..	..	..	..	..	4·9	0·018±0·006
Devikot Tube Well	(*a*)	..	..	..	..	2·1	0·015±0·004	..	..
	(*b*)	..	..	..	..	2·2	0·02±0·005	..	..
Neran Dug Well	(*a*)	..	..	..	..	5·1	0·033±0·01	..	..
	(*b*)	..	..	..	..	..	..	7·0	0·036±0·005
Ganges River Water	(*a*)	13·9	0·14±0·01	..	..	..	..	..	..
	(*b*)	..	..	..	..	14·2	0·13±0·02	..	..
Pilvai Tube Well	(*a*)	1·3	0·017±0·008	..	..	..	..	..	..
	(*b*)	..	..	..	..	..	..	5·1	0·03±0·012
Mulund Tube Well	(*a*)	10·3	0·09±0·02	..	..	..	..	..	..
	(*b*)	..	..	..	..	1·2	0·06±0·02	..	..
Shankarapura Tube Well	(*a*)	1·3	0·016±0·002	..	..	..	..	..	..
	(*b*)	..	..	2·3	0·014±0·001	..	..	..	..

a and *b* denote 1st and 2nd milking respectively. Errors quoted are due to counting statistics only.

See table 2 for details of samples, especially for Mulund Tube Well where ^{32}P activities differ in (*a*) and (*b*) significantly.

beta activity of each sample is plotted as a function of $e^{-\lambda t}$ (λ, decay constant of $^{32}P = 0{\cdot}0485\ d^{-1}$). The difference between the gross counting rates at $e^{-\lambda t} = 1$ and $e^{-\lambda t} = 0$ gives the net ^{32}P counting rate of the sample, from which the activity of ^{32}Si is calculated[8,12].

Relevant details of the surface and underground water samples analysed in this study are given in table 2. Each sample is milked twice, once using either one or both the improved techniques and the other using the earlier ones. The net ^{32}P activities and the ^{32}Si concentrations of all samples by the two separate milkings are given in table 3. The agreement between the results of the two milkings is good within the experimental uncertainties. The advantages due to the improvements are:

(*i*) Improvement in the chemical recovery of ^{32}P, from 75% to 90%.

(ii) A net saving of two days time in milking the sample increases the ^{32}P activity by about 9% at the time of first counting.

(iii) A factor of two increase in the counting efficiency of ^{32}P activity.

All in all, there is a gain of over a factor of 2·5 to 3 in the net ^{32}P activity measured if both the hydrofluorization and 4π counting techniques are employed. This enables a reliable measurement of very low ^{32}Si specific activity, *i.e.*, about 0·1 dpm in 10 metric tons of groundwater.

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