Note

PRODUCTION OF ^{34}S LABELED GYPSUM ($Ca^{34}SO_4.2H_2O$)

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ABSTRACT: Agricultural gypsum ($CaSO_4.2H_2O$) stands out as an effective source of calcium and sulfur, and to control aluminum saturation in the soil. Labeled as ^{34}S it can elucidate important aspects of the sulfur cycle. $Ca^{34}SO_4.2H_2O$ was obtained by chemical reaction between $Ca(OH)_2$ and $H_2{}^{34}SO_4$, performed under slow agitation. The acid was produced by ion exchange chromatography using the Dowex 50WX8 cation exchange resin and a $Na_2{}^{34}SO_4$ eluting solution. After precipitation, the precipitate was separated and dried in a ventilated oven at 60ºC. From 2.2 L H_2SO_4 0.2 mol L^{-1} and 33.6 g $Ca(OH)_2$, 73.7 ± 0.6 g $Ca^{34}SO_4.2H_2O$ were produced on average in the tests, representing a mean yield of 94.6 ± 0.8%, with 98% purity. The $^{34}SO_2$ gas was obtained from $Ca^{34}SO_4.2H_2O$ in the presence of $NaPO_3$ in a high vacuum line and was used for the isotopic determination of S in an ATLAS-MAT model CH-4 mass spectrometer.

Key words: sulfur 34, stable isotope, isotopic determination

PRODUÇÃO DE GESSO ($Ca^{34}SO_4.2H_2O$), MARCADO COM ^{34}S

RESUMO: O gesso agrícola ($CaSO_4.2H_2O$) destaca-se como fonte eficiente de cálcio e enxofre e na redução da saturação de alumínio no solo. O ^{34}S como traçador isotópico pode elucidar aspectos importantes no ciclo do enxofre. Para tanto o $Ca^{34}SO_4.2H_2O$ foi obtido por reação química entre o $Ca(OH)_2$ e solução de $H_2{}^{34}SO_4$, realizada sob agitação lenta. O ácido foi produzido por cromatografia de troca iônica, utilizando resina catiônica Dowex 50WX8 e solução eluente de $Na_2{}^{34}SO_4$. Após a precipitação foi separado o precipitado e realizada a secagem em estufa ventilada à temperatura de 60ºC. Nos testes, a partir de 2,2 L de H_2SO_4 0,2 mol L^{-1} e 33,6 g de $Ca(OH)_2$, foram produzidos em média 73,7 ± 0,6 g de $Ca^{34}SO_4.2H_2O$ representando um rendimento médio de 94,6 ± 0,8%, com pureza de 98%. A partir do $Ca^{34}SO_4.2H_2O$ na presença de $NaPO_3$, em linha de alto vácuo, obteve-se o gás $^{34}SO_2$ utilizado para a determinação isotópica do S no espectrômetro de massas ATLAS-MAT modelo CH-4.

Palavras-chave: enxofre 34, isótopo estável, determinação isotópica

INTRODUCTION

Gypsum is widely used in agriculture as an important nutrient input to obtain productivity increase. This compound has a two-fold function, as an effective source of calcium and sulfur, and as an aluminum saturation reducer in deeper soil layers (Vitti & Malavolta, 1985; Paolinelli et al., 1990). Gypsum is used notably in the recovery of soils with excess of sodium in order to improve root environment of acid subsoils, and is based upon the ion exchange reaction of calcium with sodium in the soil (Raij, 1988; Malavolta, 1979).

Sulfur presents four stable isotopes: ^{32}S, ^{33}S, ^{34}S, and ^{36}S, with natural abundances of 95.02; 0.75; 4.21; and 0.02 (atom %), respectively (Krouse et al., 1996). Most studies performed to date using S as a tracer have employed the ^{35}S radioisotope; this has been very useful in studies involving the dynamics of this nutrient (Lal & Dravid, 1990; Arora et al., 1990; Sharma & Kamath, 1991; Bansal & Motiramani, 1993; Patnaik & Santhe, 1993; Fitzgorald et al., 1999). However, compounds labeled with the ^{34}S stable isotope present some advantages over the radioisotope, including the following: they are not radioactive; the experiments are not limited by time; there is no exposition to radiation; and no safety measures against radiation are required.

At present, the international tendency of using non-radioactive techniques whenever possible in isotopic tracer experiments must not be forgotten, especially in field work (Zhao et al., 2001). The first studies using the ^{34}S isotopic tracer were developed by Hamilton et al. (1991) and Awonaike et al. (1993), and in Brazil by Trivelin et al. (2002).

Recently, laboratories in the USA and Europe started to produce ^{34}S highly-enriched compounds, however, at prohibited prices. In Brazil, the first studies targeted to sulfur isotope separation (especially ^{34}S) were initiated by Bendassolli et al. (1997). They used the exchange reaction between a H_2SO_3 solution ($SO_{2\ aq}$) and bisulfite anions (HSO_3^-) adsorbed to anion resins of the quaternary ammonium type. Obtaining enriched aqueous $^{34}SO_2$ allowed the production of several compounds labeled with this isotope, including: $Na_2{}^{34}SO_4$; $(^{15}NH_4)_2{}^{34}SO_4$; $K_2{}^{34}SO_4$; $Ca^{34}SO_4.2H_2O$; and $H_2{}^{34}SO_4$, among others (Maximo et al., 2000; Rossete, 2002). With such products available, the production of ^{34}S ($Ca^{34}SO_4.2H_2O$) isotope-labeled gypsum was possible, here made through the reaction between $H_2{}^{34}SO_4$ and $Ca(OH)_2$ which is the objective of this note.

MATERIAL

Equipment

ATLAS-MAT, model CH4 mass spectrometer (120° radius of tube curvature; electronic impact ionization; molecular-flow admission system; simple, Faraday-cup ion collector; and mass scan analysis system).

Pyrex glass and quartz Vacuum line; model 2M8 EDWARDS mechanical vacuum pump; model E050 EDWARDS high vacuum diffusion pump; AGD EDWARDS active vacuum gauge; APG-M EDWARDS Pirani vacuum sensor filament.

Reagents

The following reagents, all of analytical grade, were used: sulfuric and hydrochloric acid; barium and calcium chloride; barium and calcium sulfate; calcium and sodium hydroxide; and monobasic sodium phosphate. Solutions were prepared with deionized water obtained by ion exchange (5-10 mΩcm resistively).

Other material used: Dowex 50WX8 cation resin with the specifications: acid type polystyrene-divinilbenzene with 8% of DVB; sulfonic functional group; mesh 100-200.

METHODS

Production of $H_2{}^{34}SO_4$ in Dowex 50W-X8 cation resin columns

$H_2{}^{34}SO_4$ was obtained by cation exchange chromatography, using an acrylic column 130 cm height and 2.1 cm diameter (system 1), and a second acrylic column of 50 cm height and 1.5 cm diameter (system 2), filled with cation resin.

The active sites of the resin were saturated with the $R\text{-}H^+$ form by admitting 1.0 mol L^{-1} H_2SO_4 solution at the top of the column at a flow rate of 1 to 2 $cm^3\ cm^{-2}\ min^{-1}$. The resin saturation status and the volume of H_2SO_4 solution to saturate the resin with the $R\text{-}H^+$ form were determined by titration with a NaOH 0.1 mol L^{-1} solution in collected effluent volumes. Next, the excess acid remaining in the interstitial pores of the resin was eliminated with deionized water and later decompaction with water in a backwash process.

In the next step, a $Na_2{}^{34}SO_4$ 30 g L^{-1} eluting solution of enrichment of 5.85 ± 0.01%, was admitted with substitution of H^+ by Na^+ ions, producing $H_2{}^{34}SO_4$ in the eluted solution. In the H^+ elution step, the eluted volume was collected in 100 ml (system 1) or 25 ml batches (system 2); the H^+ concentration in each fraction was determined by titration with 0.1 mol L^{-1} NaOH tritisol. This procedure allowed the determination of the $H_2{}^{34}SO_4$ mass that could be obtained in each column system.

The sodium sulfate solution ($Na_2{}^{34}SO_4$) enriched at 5.85 ± 0.01 atoms % of ^{34}S was produced at the USP/CENA Stable Isotope Laboratory.

Production of ^{34}S-labeled $Ca^{34}SO_4.2H_2O$

The gypsum ($Ca^{34}SO_4.2H_2O$) was obtained from the stoichiometric ratio of the chemical reaction between $Ca(OH)_2$ and the addition of the ^{34}S-labeled $H_2{}^{34}SO_4$ solution.

In order to perform the $Ca^{34}SO_4.2H_2O$ production tests by the chemical reaction between $H_2{}^{34}SO_4$ and $Ca(OH)_2$, a H_2SO_4 solution with natural isotopic abundance was used (4.22 atoms % of ^{34}S) but with a concentration of the acid similar to that obtained by ion exchange chromatography. The nomenclature of the isotopic reagent labeling had the objective of identifying the labeling source in the process to obtain $Ca^{34}SO_4.2H_2O$; however, when the same physicochemical parameters are maintained, the process for the production of labeled $Ca^{34}SO_4.2H_2O$ must be reproduced when ^{34}S-enriched compounds are used.

The reaction was performed under slow agitation. Because of the low solubility of gypsum ($Ca^{34}SO_4.2H_2O$) in water (2.5 g L^{-1}), precipitation begins after the solubility product is reached ($Ksp = 1.0.10^{-5}$). The gypsum formation reaction can be observed in equation (1).

$$Ca(OH)_{2(s)} + 2H^+_{(aq)} + {}^{34}SO_{4\ (aq)}^{2-} \rightarrow Ca^{34}SO_4.2H_2O_{(s)} \quad (1)$$

where: (aq) and (s) indicate the aqueous and solid phases, respectively.

After precipitation, the liquid (supernatant) and the solid (precipitate) phases were separated. The solid phase was dried in a ventilated oven at 50ºC and the gravimetric quantification of the $Ca^{34}SO_4.2H_2O$ mass was made.

A small fraction of precipitate was solubilized in 50 mL deionized water, and the S-SO_4^{2-} concentration was determined by the turbidimetric method (Raij et al., 2001; Malavolta et al., 1997).

The S-SO_4^{2-} concentration was obtained from the absorbance values (spectrophotometer), using a calibration curve obtained from S-Sulfate standards (5 to 20 mg L^{-1}). This procedure allowed the calculation of the yield of the reaction by which $Ca^{34}SO_4.2H_2O$ was obtained, as well as its chemical purity.

The amount of soluble sulfate at the solution phase (supernatant) was also obtained by turbidimetry. The objective of this step was to quantify the soluble $Ca^{34}SO_4.2H_2O$ concentration and then balance the mass of the reaction in relation to sulfur.

Sample preparation for the isotopic determination

A $Ca^{34}SO_4.2H_2O$ sample of about 10.0 mg (approximately 1.8 mg S), together with sodium metaphosphate ($NaPO_3$) was placed in a quartz tube (Q1) of approximately 30 cm (Figure 1). The ratio between the $Ca^{34}SO_4.2H_2O$ mass and the reagent ($NaPO_3$) was 1:3 (w/w) (Halas & Wolacewicz, 1981). This step has the purpose of obtaining $^{34}SO_2$ gas from $Ca^{34}SO_4.2H_2O$ to determine the ^{34}S isotopic abundance (atoms % of ^{34}S) by mass spectrometry.

The $NaPO_3$ was obtained burning the $NaH_2PO_4.H_2O$ in a muffle for 2 hours at 200ºC. This step is performed to remove the structural water from the compound and to eliminate possible organic impurities. Equation (2) shows the process by which $NaPO_3$ is obtained.

$$NaH_2PO_4.H_2O \underset{\substack{\uparrow \\ \triangle}}{\overset{\substack{200^{\circ}C \\ \downarrow}}{\rightarrow}} NaPO_3 + 2H_2O \qquad (2)$$

A 2 g copper metal ring was added approximately 2 cm above the mixture (sample/reagents) using quartz wool. The metal copper is used to retain oxides formed during combustion and to convert possible SO_3 into SO_2, avoiding isotopic fractionation (Yanagisawa & Sakal, 1983; Rafter, 1957).

Next, the QT tube was connected to the high vacuum line and vacuum was established in the entire system using mechanical (MP) and diffusion pumps (DP). Traps Tr_1 and Tr_2 were later supplied with a dry ice and ethanol mixture (73ºC) or with liquid nitrogen (-196ºC), respectively. The Tr_1 and Tr_2 traps are designed to trap water and SO_2 vapors, respectively, formed during combustion. The high vacuum line to obtain SO_2 adapted from Bailey & Smith (1972) can be observed in Figure 1.

In the next step, the MF oven heated to 900ºC was displaced vertically up to the QT tube, where it remained for a 10-minute interval during which the $Ca^{34}SO_4.2H_2O$ combustion occurred in the presence of reagents, forming the SO_2 gas (equation 3). Depending on the conditions (O_2 partial pressure), the SO_3 gas can be produced (equation 4). The formation of SO_3 is not desirable, since it can cause isotopic fractionation. Equation 5 shows the conversion of SO_3 to SO_2 via reduced copper.

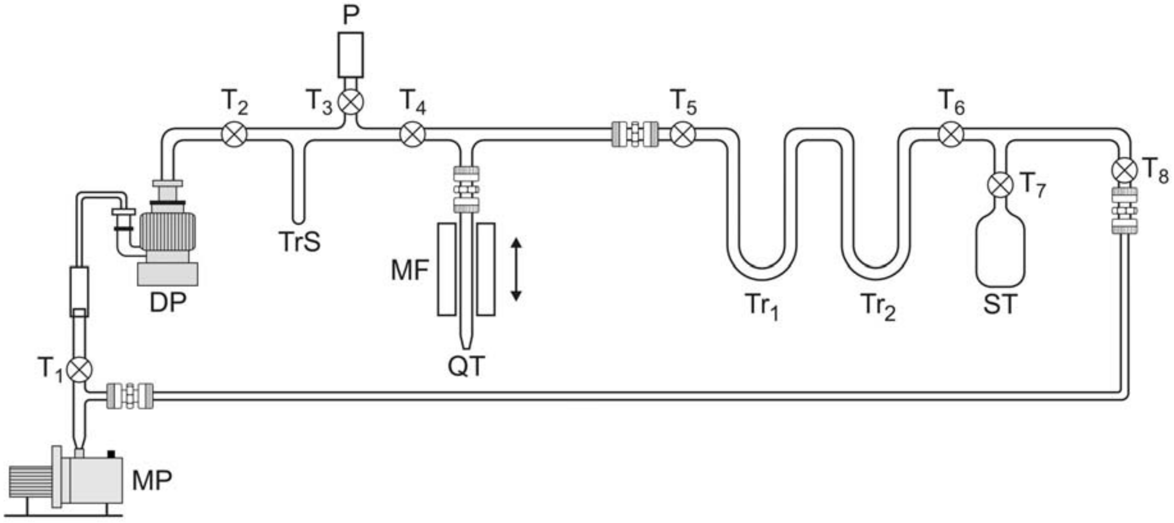

Figure 1 - High vacuum line used in the production and purification of SO_2. QT = quartz tube; MF = movable furnace (900 ºC); Tr_1 = trap containing dry ice plus ethanol (-73 ºC); Tr_2 = trap containing liquid nitrogen (-196 ºC); ST: stock sample tube; P = Pirani vacuum gauge filament sensor (Edwards); TrS = security trap containing liquid nitrogen (-196 ºC); DP = diffusion pump (high vacuum); MP = mechanical pump (previous vacuum); T_1 to T_8 = Taps.

$$Ca^{34}SO_4.2H_2O + NaPO_3 \underset{\overset{\uparrow}{\triangle}}{\overset{\overset{900^{o}C}{\downarrow}}{\rightarrow}} NaCaPO_4 + SO_{2(g)} + 1/2O_{2(g)} + 2H_2O \tag{3}$$

$$SO_{2(g)} + 1/2O_{2(g)} \rightleftharpoons SO_{3(g)} \tag{4}$$

$$SO_{3(g)} \quad + \quad Cu^0 \underset{\overset{\uparrow}{\triangle}}{\overset{\overset{900^{o}C}{\downarrow}}{\rightarrow}} SO_{2(g)} + CuO \tag{5}$$

The SO_2 gas entrapped in Tr_2 was then transferred to the sample tube (ST), by alternating the liquid N_2 ("trap") from Tr_2 into the sample tube (ST).

Later, sample tube (ST) containing the SO_2 gas was transferred from the high vacuum line and connected to the mass spectrometer admission system and the isotopic determination of S was made (atoms % of ^{34}S).

The QT tube was cleaned after combustion of the sample in the high vacuum line. Initially, the quartz wool was removed from the oxidized copper ring (CuO), and the oxidized copper was then transferred to a glass container for later reduction (Cu^0) in a vacuum line using hydrogen (Bendassolli et al., 2002).

Finally, the QT tube was scraped to remove residues from the reaction, and washed with HCl 6.0 mol L^{-1} so it could be reused in other combustions.

Isotopic determination of S

The mass spectrometry analysis of isotopic ratios or atoms % (abundance) of light elements, for the most part, is made on properly purified gaseous samples, and in a low- or medium-resolution-power mass spectrometer. To accomplish this, the sample preparation system involves some chemical transformations, and gases free from any atmospheric contaminant are required for their production.

For the isotopic determination of S in the SO_2 gas samples contained in the storage flasks, the mass spectrometer worked with a heated admission system (70ºC) due to the polar nature of the SO_2 and SO molecules, avoiding a memory effect between analyses.

A cryogenic trap containing dry ice and ethanol (-73ºC) was adapted on the mass spectrometer admission system, in order to retain water contained in the gas samples.

The abundance determination in atoms % of ^{34}S in SO_2 samples was performed in mass spectrometer according to Bendassolli et al., 1997.

RESULTS

The preliminary $H_2{}^{34}SO_4$ production tests were performed with natural $Na_2{}^{34}SO_4$. The labeled-$H_2{}^{34}SO_4$ production process must be reproduced, because the physicochemical parameters must be preserved when enriched ^{34}S-isotope compounds are used.

In the process of production of $H_2{}^{34}SO_4$ using the 2.1 cm diameter (130 cm height) acrylic column, 3.0 L of H_2SO_4 solution were required for complete saturation of the active sites of the resin to the $R\text{-}H^+$ form; 2.2 L deionized water were needed to eliminate the excess acid from the resin interstitial volume. Resin decompaction was performed later with deionized water.

In system 1, containing 426 cm^3 cation resin in the $R\text{-}H^+$ form (wet, balanced in water) 2.2 L $Na_2{}^{34}SO_4$ 30 g L^{-1} solution was used for total elution of the H^+ ions, and a final solution containing 44.2 g $H_2{}^{34}SO_4$ in 2.2 L (0.2 mol L^{-1}) was obtained.

The chemical reaction of $H_2{}^{34}SO_4$ with $Ca(OH)_2$ was performed at a stoichiometric ratio. The tests were performed in three replications using the same acid, but on different days. We used 2.2 L $H_2{}^{34}SO_4$ in each test at a concentration of 0.2 mol L^{1}, and 33.6 g $Ca(OH)_2$ were added slowly, theoretically forming a precipitate containing approximately 78.0 g $Ca^{34}SO_4.2H_2O$.

The $Ca^{34}SO_4.2H_2O$ mass produced in each test was determined in the precipitate by a gravimetric method. Using the theoretical value for the $Ca^{34}SO_4.2H_2O$ mass (78.0 g) and the mass obtained experimentally in the chemical reaction, the reaction yield and total mass of $Ca^{34}SO_4.2H_2O$ lost in the process could be calculated. Table 1 shows the $Ca^{34}SO_4.2H_2O$ mass produced, losses, and chemical reaction yields in each test. It can be observed that complete $Ca^{34}SO_4.2H_2O$ precipitation did not occur in any of the three tests. On average, 73.7 ± 0.6 g $Ca^{34}SO_4.2H_2O$ were produced in these tests, representing a mean yield of 94.6 ± 0.8%. There was no pronounced variability in $Ca^{34}SO_4.2H_2O$ mass loss; on average, this fraction represented 5.4 ± 0.8%. This is a relatively high value, since it is a labeled material with high added value.

Because complete gypsum precipitation did not occur, the supernatant of each test was analyzed in order to determine the mass lost in the reaction. The pH readings in the supernatant were in the range of 6.0 to 7.0, possibly indicating the complete consumption of $H_2{}^{34}SO_4$ in the chemical reaction with $Ca(OH)_2$. Therefore, the H^+ concentration in the solution (supernatant) was very reduced (10^{-6} to 10^{-7} mol L^{-1}).

The S-$^{34}SO_4^{2-}$ concentration in the supernatant was measured in the three tests, to estimate the $Ca^{34}SO_4.2H_2O$ mass solubilized in the volume. The data shown in Table 1 demonstrates that part of the 2.7 g $Ca^{34}SO_4.2H_2O$ not recovered in the chemical process were present in the supernatant volume. This solubilized $Ca^{34}SO_4.2H_2O$ fraction can be recovered in the chemical reaction process using ^{34}S-enriched $H_2{}^{34}SO_4$.

From the results presented in Table 1, it can be verified that the $Ca^{34}SO_4.2H_2O$ mass lost in the chemical process was 1.5 g on average. Also, using the results from Table 1, the global mass balance for the chemical reaction process between $H_2{}^{34}SO_4$ and $Ca(OH)_2$ to produce $Ca^{34}SO_4.2H_2O$ can be obtained. The mean for the global mass balance process can be observed in Table 2.

It can be observed from Table 2 that, on average, 64.3% of the $Ca^{34}SO_4.2H_2O$ losses of the chemical reaction process occurred in the supernatant, while 35.7% were not identified. From the same Table, it can be verified that only 2% of the total mass ($Ca^{34}SO_4.2H_2O$) was really lost, which makes the process viable when ^{34}S is used.

From the result presented in Table 2 it can also be observed that 3.4% of the $Ca^{34}SO_4.2H_2O$ mass lost in the process is solubilized in the supernatant, with a value equivalent to 50.2 mg ^{34}S.

The S-SO_4^{2-} concentration in the $Ca^{34}SO_4.2H_2O$ obtained through the chemical process (three assays) was determined by turbidimetry, indicating a purity of produced $Ca^{34}SO_4.2H_2O$ of 98%, on average.

The test using the ^{34}S-labeled $Na_2{}^{34}SO_4$ solution with an abundance of 5.85 ± 0.01 atoms % performed in system 2, containing 33 cm^3 cation resin in the R-H^+ form (balanced in water) allowed to obtain about 3.0 g of ^{34}S-labeled $H_2{}^{34}SO_4$.

From the chemical reaction between labeled $H_2{}^{34}SO_4$ and $Ca(OH)_2$, under stoichiometric conditions, 5.2 g $Ca^{34}SO_4.2H_2O$ could be obtained in theory. The mass obtained in the reaction was 4.8 g $Ca^{34}SO_4.2H_2O$, with a 91% yield.

The ^{34}S determination in atoms % of ^{34}S was performed on three replicates for each test. For the evaluation of isotopic results a natural variation from -30 to +30‰ was taken into consideration (Krouse & Tabatabai, 1986). The natural variation values (-30 to +30‰) correspond to a variation from 4.15 to 4.38 atoms % of ^{34}S. It must also be considered that the analytical precision of the mass spectrometer is in the order of 1%.

The results for isotopic determination of S in the SO_2 gas samples obtained from the three $Ca^{34}SO_4.2H_2O$ production tests (natural abundance), one $CaSO_4.2H_2O$ p.a. sample (natural abundance), and ^{34}S-labeled $Ca^{34}SO_4.2H_2O$ test can be observed in Table 3.

The values presented in Table 3 concerning samples ($CaSO_4.2H_2O$) with natural variation, labeled material, or the p.a. product, are in accordance with the expected values (4.15 to 4.38 atoms % of ^{34}S), demonstrating that the process for obtaining SO_2 in the presence of $NaPO_3$ and the isotopic determination of S in the mass spectrometer were suitable.

Table 1 - $Ca^{34}SO_4.2H_2O$ mass produced, losses, and yield (%) of the chemical reaction.

Tests	Mass produced	Losses*	Supernatant mass	Yield
	g			%
1st	73.9	4.1	2.9	94.7
2nd	73.1	4.9	2.6	93.7
3rd	74.2	3.8	2.5	95.2
Mean ± se	73.7 ± 0.6	4.2 ± 0.6	2.7 ± 0.2	94.6 ± 0.8

*Difference between theoretical $Ca^{34}SO_4.2H_2O$ mass (78.0 g) and experimentally†obtained values.

Table 2 - Global balance for the chemical reaction process to obtain $Ca^{34}SO_4.2H_2O$.

Tests	Chemical reaction yield	$Ca^{34}SO_4.2H_2O$ losses in the process	Non-recovered fraction	
			Supernatant $Ca^{34}SO_4.2H_2O$	Lost $Ca^{34}SO_4.2H_2O$*
	%			
1st	94.75	5.25	3.76	1.49
2nd	93.75	6.25	3.37	2.88
3rd	95.22	4.78	3.15	1.63
Mean ± se	94.6 ± 0.8	5.4 ± 0.8	3.4 ± 0.3	2.0 ± 0.77

*% $Ca^{34}SO_4.2H_2O$ required to complete the balance (not identified).

Table 3 - Isotopic determination of S, (atoms % of ^{34}S), directly from $Ca^{34}SO_4.2H_2O$ in the presence of $NaPO_3$.

Samples	S determination (atoms % of ^{34}S)
1st test	4.34 ± 0.01
2nd test	4.34 ± 0.02
3rd test	4.34 ± 0.02
$CaSO_4.2H_2O$ p.a.	4.33 ± 0.04
Labeled $Ca^{34}SO_4.2H_2O$	5.85 ± 0.03

The result for isotopic determination of S (atoms % of ^{34}S) in the test that used labeled material ($Na_2{}^{34}SO_4$ 5.81 ± 0.01 atoms % of ^{34}S) demonstrated that there was no isotopic fractionation in the process for the production of ^{34}S-labeled $Ca^{34}SO_4.2H_2O$.

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