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**An Explanation of the Divergency between  $^{34}\text{S}/^{32}\text{S}$  Measurements  
on  $\text{SO}_2$  and  $\text{SF}_6$ .**

Wyjaśnienie rozbieżności między pomiarami  $^{34}\text{S}/^{32}\text{S}$  z użyciem  $\text{SO}_2$  i  $\text{SF}_6$ .

Выяснение разницы между измерениями  $^{34}\text{S}/^{32}\text{S}$  в  $\text{SO}_2$  и  $\text{SF}_6$ .

Dedicated to Professor  
Stanisław Szpikowski on occasion  
of his 60th birthday

INTRODUCTION

The Third Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations [1] revealed that the consistency of sulphur isotope determinations among different laboratories is unsatisfactory. Reasons for this poor agreement were investigated by Rees [2] who compared sulphur isotope measurements using  $\text{SO}_2$  and  $\text{SF}_6$ . He reported that  $\delta^{34}\text{S}$  values obtained for ocean water sulphate were 20.3 and 21.0 permil, respectively [3].

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This difference is partially caused by the adsorption of  $\text{SO}_2$  gas on the walls of the inlet tube and parts of the ion source. For the mass spectrometer used by Rees [2], measurements taken 60 s after switching between the standard and unknown, required a memory correction factor of 1.016. Reasons for the remaining difference in values obtained by the two techniques (a factor  $1.034/1.016 = 1.018$ ) were not clear.

The  $\text{SF}_6$  scale is more accurate and reliable because of the simplicity of the  $\text{S}^{19}\text{F}_5^+$  mass spectrum which comprises about 90 percent of the total ion species. In contrast,  $\text{SO}_2^+$  comprises about 50 percent of the total ion species and the spectrum is complicated by overlapping due to oxygen isotopes, e.g.  $^{32}\text{S}^{16}\text{O}^{18}\text{O}^+$  which is not resolved from  $^{34}\text{S}^{16}\text{O}_2^+$ .

Since the effect of oxygen isotopes can be satisfactorily corrected, other factors must be responsible for the bias in  $\delta^{34}\text{S}$  values obtained using  $\text{SO}_2$  gas. Two factors which will be considered in this paper are contributions to  $m/e = 64$  and  $66$  peaks from  $\text{S}_2^+$  and the proton-containing species  $\text{HSO}_2^+$  and  $\text{H}_2\text{SO}_2^+$ .

### $\text{S}_2^+$ EFFECT

Evidence that  $\text{S}_2^+$  species may form, arises from the high peak of  $m/e = 80$  always observed in the spectrum of pure  $\text{SO}_2$ . This peak is identified with  $\text{S}_2\text{O}^+$ . However, it can be readily shown that the  $\text{S}_2^+$  contribution to the major peak ( $m/e = 64$ ) is greater than to the minor peak ( $m/e = 66$ ); the effect is opposite to the result we wish to explain because it will produce slightly higher measured  $\delta_m^{66}$  values, as shown below.

In order to derive the relation between the corrected  $\delta^{34}\text{S}$  and  $\delta_m^{66}$  values let us consider the following two values

$$C = \frac{\text{S}_2^+ \text{ contribution at mass 64}}{\text{SO}_2^+ \text{ contribution at mass 64}}; \quad \text{and} \quad (1)$$

$$\eta = \frac{R^{34}}{R^{66}} = \frac{R^{34}}{R^{34} + 2R^{18} + 2R^{33}R^{17}} \approx \frac{\frac{1}{22.5}}{\frac{1}{22.5} + \frac{2}{490} + \dots} \quad (2)$$

where  $R^a$  signifies the appropriate abundance ratios:  $R^{34} = {}^{34}\text{S}/{}^{32}\text{S}$ ,  $R^{18} = {}^{18}\text{O}/{}^{16}\text{O}$ ,  $R^{33} = {}^{33}\text{S}/{}^{32}\text{S}$  and  $R^{17} = {}^{17}\text{O}/{}^{16}\text{O}$ ; this useful notation is adopted from the paper by Mook and Grootes [4].

For the measured ratio of an unknown sample one may write

$$R_m^{66} = \frac{\text{SO}_2^+ \text{ at } 66 + \text{S}_2^+ \text{ at } 66}{\text{SO}_2^+ \text{ at } 64 + \text{S}_2^+ \text{ at } 64} \quad (3)$$

Using (1) and the definition of delta value the above formula may be rewritten as

$$R_m^{66} = \frac{R^{66} + 2 \left(1 + \frac{\delta^{34}}{10^3}\right) R_s^{34} C}{1 + C} \quad (4)$$

Similar formula for the standard gas is

$$(R_m^{66})_s = \frac{R_s^{66} + 2R_s^{34} C}{1 + C} \quad (5)$$

Therefore

$$\frac{R_m^{66}}{(R_m^{66})_s} = 1 + \frac{\delta^{66}}{10^3} = \frac{\frac{R^{66}}{R_s^{66}} + 2 \left(1 + \frac{34}{10^3}\right) \eta C}{1 + 2\eta C} \quad (6)$$

where  $\delta^{34}\text{S}$  may be calculated from the unbiased  $\delta^{66}$  value by using the oxygen correction factor [5]

$$C_{\text{oxygen}} = \left(1 + 2 \frac{R^{18}}{R_s^{34}}\right)^{-1} = 1.09 \quad (7)$$

From (6) and (7) we may write

$$\delta^{34}_S = \frac{1 + C_0}{1.09 + C_0} \delta_m^{66}, \quad (8)$$

where  $C_0 = 2\eta C \approx 2C$ . According to this equation the ratio  $\delta^{34}_S$  to  $\delta_m^{66}$  is smaller than the oxygen correction factor. For example, if  $S_2^+$  production is 5%, which corresponds to  $C_0 = 0.1$ , the ratio  $\delta^{34}_S/\delta_m^{66} = 1.08$ . Since the larger production than 5% is rather unlikely, then the effect of  $S_2^+$  production on the bias in mass spectrometric measurements is meaningless.

#### EFFECT OF $HSO_2^+$ AND $H_2SO_2^+$

Let us consider the contributions of the proton-containing species  $H^{33}SO_2^+$  and  $H_2^{32}SO_2^+$  to the minor peak of  $m/e = 66$ . The production rate of these species is proportional to the ion beam intensities at mass 65 and 64, respectively, i.e.

$$\langle HSO_2^+ \rangle = k_1 \cdot I^{65}, \quad (9)$$

$$\langle H_2SO_2^+ \rangle = k_2 \cdot I^{64}. \quad (10)$$

The measured ratio for an unknown sample is

$$\begin{aligned} R_m^{66} &= \frac{I^{66} + k_1 \cdot I^{65} + k_2 \cdot I^{64}}{I^{64}} \\ &= R^{66} + k_1 \cdot R^{65} + k_2 \\ &= R^{66} + k_1 \left(1 + \frac{\delta^{65}}{10^3}\right) R_S^{65} + k_2. \end{aligned} \quad (11)$$

Similar formula for standard is

$$(R_m^{66})_S = R_S^{66} + k_1 R_S^{65} + k_2. \quad (12)$$

Dividing (11) by (12), one obtains

$$1 + \frac{\delta_m^{66}}{10^3} = \frac{1 + \frac{\delta^{66}}{10^3} + k_1 \left(1 + \frac{\delta^{65}}{10^3}\right) \frac{R_s^{65}}{R_s^{66}} + \frac{k_2}{R_s^{66}}}{1 + k_1 \frac{R_s^{65}}{R_s^{66}} + \frac{k_2}{R_s^{66}}} \quad (13)$$

In order to simplify this equation let us denote

$$C_1 = k_1 \frac{R_s^{65}}{R_s^{66}}, \quad \text{and} \quad (14)$$

$$C_2 = k_2/R_s^{66}, \quad (15)$$

then the equation (13) may be rewritten as

$$(1 + C_1 + C_2) \delta_m^{66} = \delta^{66} + C_1 \delta^{65} \quad (16)$$

Substituting here  $\frac{1}{2} \delta^{66}$  for  $\delta^{65}$ , inasmuch as the isotope separation is approximately proportional to mass difference, we obtain the following expression for the corrected value

$$\delta^{66} = \frac{1 + C_1 + C_2}{1 + C_1/2} \delta_m^{66}. \quad (17)$$

Assuming a similar production rate of both species,  $k_1 \approx k_2$  we may estimate from (14) and (15) that  $C_1 \ll C_2$ , thus

$$\delta^{66} = (1 + C_1/2 + C_2) \delta_m^{66}, \quad (18)$$

and

$$\delta^{34S} = 1.09(1 + C_1/2 + C_2) \delta_m^{66}. \quad (19)$$

## DISCUSSION

In the derived formula (18) the correction for  $\text{HSO}_2^+$  production is represented by term  $C_1/2$  which, according to definition (14), may be estimate as 0.016  $k_1$ . In contrast, the correction for  $\text{H}_2\text{SO}_2^+$  production

$$C_2 = \frac{k_2}{22}$$

is significant even at very low production rate of this species. Considering  $k_2$  to be only one part per thousand, we obtain  $C_2 = 0.022$  which may totally explain the observed discrepancy between  $\text{SO}_2$  and  $\text{SF}_6$  scales!

The mechanism of formation of the proton-containing species was not investigated yet. These species may be formed by ionization and dissociation of  $\text{H}_2\text{SO}_3$  molecules and, indirectly, as result of ion-molecule reactions. In the second way are formed ions  $\text{H}_3^+$  and  $\text{H}_3\text{O}^+$ , always present in mass spectra.

The postulated species  $\text{HSO}_2^+$  and  $\text{H}_2\text{SO}_2^+$  must be detected using either high resolution mass spectrometry or, indirectly, by studying the influence of water vapour and  $\text{H}_2$  gas on low resolution spectra.

Preliminary results using the second approach are consistent with the existence of such species. These results may be summarized as follows: (1) Addition of hydrogen to the sample gas causes a strong dependence of the measured delta value on the electron energy, see Fig. 1. (2) It is observed a decrease, by constant factor of 1.035, of the measured  $\delta_m^{66}$  when both capillaries are homogeneously heated to about 100°C. (3) Heating the mass spectrometer chamber after a longer period of work at room temperature causes a considerable drop of absolute value  $\delta_m^{66}$ .

Of course every one who has access to a high resolution mass spectrometer is most wellcome to investigate the components at mass 66. The high resolution spectrum this mass number is shown in Fig. 2. The resolving power of the mass spectrometer  $M/\Delta M = 10\ 000$  is desirable.

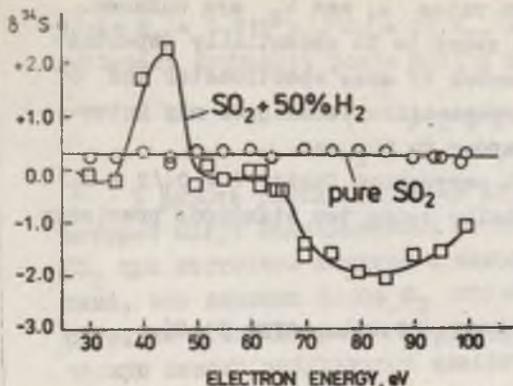


Fig. 1. Plot of measured  $\delta^{34}\text{S}$  values in permil versus electron energy in eV for a pure  $\text{SO}_2$  sample and for the same sample after addition 50%  $\text{H}_2$ .

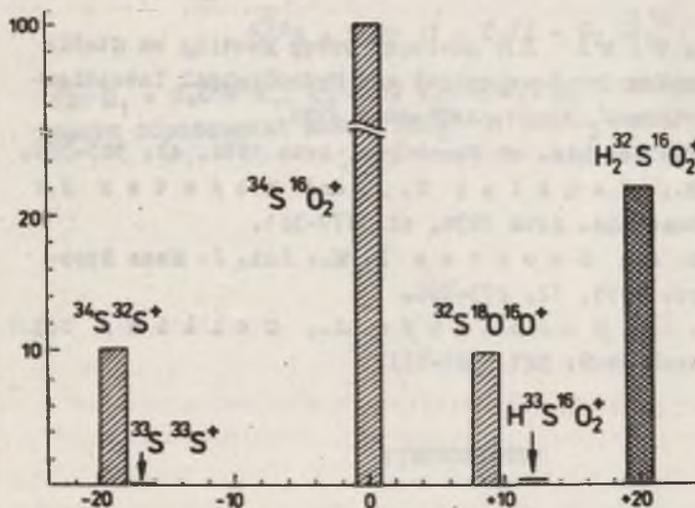


Fig. 2. Calculated high-resolution mass spectrum around  $m/e = 66$ . Abscissa values represent the difference in mass from the mass of  $^{34}\text{S}^{16}\text{O}_2^+$  molecule in  $10^{-5}$  of mass unit.

#### CONCLUSION

The effect of  $\text{S}_2^+$  production is meaningless but that of  $\text{H}_2\text{SO}_2^+$  and  $\text{HSO}_2^+$  may be totally responsible for the bias in all data obtained with  $\text{SO}_2$ . However, in correcting  $\delta_m^{66}$  for the proton-containing species the derived formula (18) is practically useless

because the relative production rates  $k_1$  and  $k_2$  are unknown. Moreover, the production rates seems to be essentially depended on vacuum conditions of the chamber of mass spectrometer and of the inlet system. Also sample preparation techniques may introduce a small amount of water vapour to  $SO_2$  gas.

For this reasons the total correction factor  $1 + C_1/2 + C_2$  should be determined experimentally using two standards precisely calibrated by the  $SF_6$  method.

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#### STRESZCZENIE

W pracy rozważono wpływ jonów  $S_2^+$ ,  $HSO_2^+$  i  $H_2SO_2^+$ , które mogą nakładać się na wierzchołek  $m/e = 66$  w widmie masowym  $CO_2$  podczas analizy izotopowej przy użyciu dwutlenku siarki. Wykazano, że wpływ jonów  $S_2$  jest nieznaczny, podczas gdy obecność jonów wodorków  $SO_2$  może całkowicie wyjaśnić systematyczny błąd wyników pomiarów  $^{34}S/^{32}S$  otrzymywanych przy użyciu  $SO_2$ . Wyprowadzono następujący wzór na poprawkę, którą trzeba wnieść do mierzonej wartości  $\delta_m^{66}$ , aby otrzymać  $^{34}S$ :

$$\delta^{34}S = 1.09 (1 + C_1/2 + C_2) \delta_m^{66}$$

gdzie  $C_1 = 0.016 k_1$ ,  $C_2 = 22 k_2$ , zaś  $k_1$  i  $k_2$  oznaczają względne szybkości produkcji jonów  $\text{HSO}_2^+$  i  $\text{H}_2\text{SO}_2^+$ .

### РЕЗЮМЕ

В работе рассматривается влияние ионов  $\text{S}_2^+$ ,  $\text{HSO}_2^+$  и  $\text{H}_2\text{SO}_2^+$  которые могут накладываться на пик  $m/e = 66$  в массовом спектре  $\text{CO}_2$  при изотопном анализе с использованием двуокиси серы. Доказано, что влияние ионов  $\text{S}_2$  незначительное, в то время как присутствие ионов гидратов  $\text{SO}_2$  может полностью объяснить систематическую ошибку результатов измерений  $^{34}\text{S}/^{32}\text{S}$ . Выведена следующая формула на поправку, которую следует ввести в измеренное значение  $\delta_m^{66}$ , чтобы получить  $\delta^{34}\text{S}$ :

$$\delta^{34}\text{S} = 1.09 (1 + C_1/2 + C_2) \delta_m^{66},$$

где  $C_1 = 0,016 k_1$ ,  $C_2 = 22 k_2$ , и  $k_1$ ,  $k_2$  - это относительные скорости образования ионов  $\text{HSO}_2^+$  и  $\text{H}_2\text{SO}_2^+$ , соответственно.

