



## Simultaneous Determination of $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$ on $\text{SO}_2$ Gas

Tomasz Pieńkos and Andrzej Pelc

M. Curie-Skłodowska University, Lublin, Poland (tomasz.pienkos@umcs.pl, andrzej.pelc@poczta.umcs.lublin.pl)

In this study we have applied  $\text{SO}_2$  gas to the multiple isotope analysis (i.e. simultaneous analysis of sulfur isotope ratios:  $^{33}\text{S}/^{32}\text{S}$ ,  $^{34}\text{S}/^{32}\text{S}$  and  $^{36}\text{S}/^{32}\text{S}$ ) using  $\text{S}^+$  ion beams. So far such analysis is performed on  $\text{SF}_6$  gas, the preparation of which requires the use of a fluorination line (Ono et al., 2006) and a mass spectrometer with enhanced resolving power to resolve isotope peaks  $^{33}\text{SF}_5$  from  $^{32}\text{SF}_5$  at masses 128 and 127. On the other hand  $\text{SO}_2$  gas can be easily prepared from sulfides and from sulfates (Halas and Wolacewicz, 1981). Moreover, a great advantage of the isotope analysis on  $\text{S}^+$  instead on  $\text{SO}^+$  or  $\text{SO}_2^+$  spectra is that there is no need to keep constant oxygen isotopic composition in the  $\text{SO}_2$  gas. Usually sulfide and sulfate samples prepared to  $\text{SO}_2$  have different oxygen, but it doesn't matter in the case of analysis on  $\text{S}^+$ .

In the patent application (Halas et al., 2016) we have described a new ion source which can be applied for analysis of gases. The new ion source significantly enhances the generation of positive and negative ions in comparison to commonly used Nier type by more than 2 orders of magnitude. The analyzed gas is admitted from a dual inlet system to the ion source through separate capillaries connected to the pneumatically operated changeover valve as described by Halas (1979). Prepared  $\text{SO}_2$  samples were purified from water and  $\text{O}_2$  which eliminates interference at mass 32 peak. Nevertheless a contamination at peak 33 was observed, most likely from hydrogen desorbed inside the vacuum system. For this reason we were not able to determine  $\delta^{33}\text{S}$ , because of formation of  $^{32}\text{SH}^+$  ions which interfere with  $^{33}\text{S}^+$ , thereby measured delta value was unstable in time. This was not the case with the smallest peak 36. The ion currents were measured as voltages on the high-ohm resistors of 0.2, 5 and 500G $\Omega$ , with respective capacitors yielding a common time constant of 1.5 s. The obtained precision ( $1\sigma$ ) on positive ion beams was better than 0.1‰ and 0.01‰ for  $\delta^{36}\text{S}$  and  $\delta^{34}\text{S}$ , respectively.

The details of the design of the innovative ion source, vacuum system, electronic controllers, results of test measurements (standard vs. standard and zero enrichment) and obtained  $\delta^{34}\text{S}$  values for IAEA sulfur isotope reference materials will be presented.

### References

- Halas S. (1979) An automatic inlet system with pneumatic changeover valves for isotope ratio mass spectrometry, *Journal of Physics E: Scientific Instruments* 12: 418-420.
- Hałas S., Pieńkos T., Pelc A., Wójtowicz A. (2016) Patent descriptions P.416375 and P.417560.
- Halas S. and Wolacewicz W. (1981) Direct extraction of sulfur dioxide from sulfates for isotopic analysis, *Analytical Chemistry* 53: 686-689.
- Ono S., Wing B., Johnston D., Farquhar J., Rumble D. (2006) Mass dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles, *Geochimica et Cosmochimica Acta* 70: 2238-2252.