

# Strategies of background lowering in high temperature-carbothermic reduction-continuous flow oxygen isotope ratio determination

Tiziano Boschetti<sup>1</sup>, Paola Iacumin<sup>1</sup> and Isabella Bombagi<sup>1</sup>

1 - Earth Sciences Department, Parma University, Parco Area delle Scienze 157/A, 43100 Parma, Italy.

<sup>\*</sup>corresponding author: tiziano.boschetti@unipr.it

## Introduction

Air blanks from solid sample introduction limit the performance of any EA system. Particularly for small and isotopically enriched samples any contribution of air affects the isotope ratio results. The bigger the blank and its isotopic difference from the sample, the greater the effect on the measured isotope value. Particularly in the on-line analysis of oxygen isotope,  $^{18}\text{O}/^{16}\text{O}$  ratio determination suffers for interference of atmospheric nitrogen ( $^{14}\text{N}$ ). In this publication we present the first results obtained with the new NoBlank solid autosampler (Thermo Electron Co.) coupled with FlashEA 1112 elemental analyzer (Thermo Electron Co.) and Delta Plus XP mass spectrometer (Thermo Electron Co.). Moreover, in order to improve the analytical condition, a new reactor with a  $-\text{SiC}$  mantle tube was tested because the currently available elemental analyzer's reactor for the measurement of the oxygen isotopic composition using CR-CF-IRMS method (carbothermic reduction - continuous flow - isotopic ratio mass spectrometry) produce amounts of background  $\text{CO}$ , with a instable baseline drifting upward proportionally to the temperature and downward to the time.



Fig. 1 - Complete Sampling Unit.

- 1 - NoBlank Sampler Device
- 2 - MAS 200R Autosampler
- 3 - FlashEA 1112 Top Cover

The new NoBlank sampling device (Fig. 1, Fig. 2 and Fig. 3) uses an innovative technique for the solid sample introduction exploiting the time of previous analysis for the purging. It does not require pre-analytic time for conditioning or after carousel addition. In the conical rotor a washing chamber is present. It is a particular shaped cavity to accommodate the sample. According to the movement of the rotating sampling system, the washing chamber has three positions: Loading, Purging and Sampling (Fig. 2).

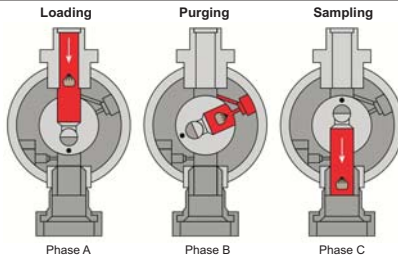


Fig. 2 - NoBlank Sampling Phases (Schematic section of the rotor, front view. Thermo Electron, 2005).

- Phase A - Loading (status LED marked L is lit): Sample coming from MAS200R carousel (Fig. 1) drops in the washing chamber.
- Phase B - Purging (status LED marked P is lit): Washing chamber is aligned to the He gas purge inlet (point 7 in Fig. 3).
- Phase C - Sampling (status LED marked S is lit): The washing chamber is aligned downward. The sample drops in the reactor.



Fig. 3 - Front view of the NoBlank Sampler Device.

- 1 - Head Body
- 2 - Sampling System and Windows
- 3 - Upper Fitting
- 4 - Carrier Gas Inlet Port
- 5 - Lower Fitting
- 6 - Pressure Gauge
- 7 - Purge Gas Inlet Port
- 8 - Pressure Regulator
- 9 - Status LEDs

The first tests were carried out using MAS200R + NoBlank autosampler + Flash 1112 EA + ConFloIII + Delta Plus XP, with the following instrument conditions: OH-side standard reactor (glassy carbon inner tube and ceramic outer tube) temperature: 1420 °C; GC moisture column temperature: 70 °C; He carrier flow (5.5 grade): 80 mL/min; He purge flow (5.5 grade): 75-100mL/min; Purge pressure on NoBlank device: 0.1-0.3 bar. Autosamplers currently commercialized without NoBlank device (AS128 and MAS200R) were also tested for comparison. The test results (Fig. 4) testify to a significantly reduced signal of atmospheric nitrogen peak (~200 s) during the use of NoBlank device (lower than 3 mV on mass 28) in comparison with standard autosamplers without NoBlank (from 20 to 44 mV on mass 28).

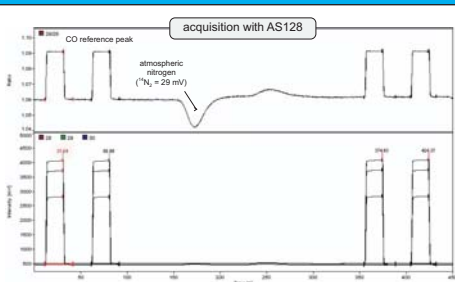


Fig. 4 - Chromatograms comparison showing the NoBlank efficacy.

The self-diffusion of Al and O in the  $\text{Al}_2\text{O}_3$ -ceramic mantle tube's reactor used for oxygen analysis is visibly demonstrated with 1) the growth of glassy-silica pockets in the outside hottest zone of ceramic tube (Fig. 5); 2) the surface alteration observed on the surface of the used glassy carbon tube which showed metallic aluminium inclusions; and 3) formation of ashes in the external surface of the glassy carbon tube visible also several days after the analysis. Ash picked from the outer surface of the glassy-carbon tube and analyzed by SEM confirmed that the compound was  $\text{Al}_2\text{O}_3$  (99 ± 1 %). In fact, it is widely demonstrated that oxygen and aluminum self-diffusion in  $\text{Al}_2\text{O}_3$  and mullite increase markedly when temperatures is above 1300 °C (Oishi and Kingery, 1960; Fielitz et al., 2001; Fielitz et al., 2004), leading to an enhanced reaction rate of mobile oxygen with carbon from the glassy carbon at the inner surface of the alumina tube (Gehre et al 2004; Boschetti and Iacumin 2005). In order to optimize the performance of the carbothermic reduction reactor, signal background must be as low as possible. To make this, problems outlined above could be solved by the use of oxygen-free ceramic material composite (CMC), possibly choosing between the materials with the best cost/benefit ratio. In this study, a high purity silicon carbide (sintered  $-\text{SiC}$ ) tube was selected as outer tube of the reactor (Fig. 6). Performance tests on the tube were executed on FlashEA 1112 elemental analyzer device (Thermo Electron), substituting the standard ceramic mantle tube with the SiC tube (17 mm o.d., 13 mm i.d., length 450 mm). The background signals of the silicon carbide reactor are significantly lower than the signals of the ceramic one. In comparison with  $\text{Al}_2\text{O}_3$ -ceramic tube, use of silicon carbide tube in the CR-CF-IRMS methods is advantageous for: i) background lowering of the CO-masses related to the oxygen isotope determination (Fig. 7); ii) stronger resistance to high temperature (maximum temperature limit is 1900°C) and thermal shock; iii) lower thermal expansion; iv) longer lifetime. The only disadvantage is connected to the high thermal conductivity:  $\sim 30 \text{ W m}^{-1} \text{ K}^{-1}$  at 1400°C for  $-\text{SiC}$  (Munro 1997), compared with  $\sim 3.8 \text{ W m}^{-1} \text{ K}^{-1}$  at 1400°C for mullite (<http://www.memsnet.org/material/mullite3al2c3sic2bulk/>), that is undesirable for a safe O-ring Viton® sealing (maximum continuous-use temperature: 204°C). This problem has been solved by positioning two fans (208-240 V, 85-75 mA, 12-11 W, 50-60 Hz) on the enclosing panel of the reactor, in front to the two junction nuts. By the fans the maximum temperature measured at the nuts was of 61°C at  $T_{\text{reactor}} = 1450^\circ\text{C}$ .

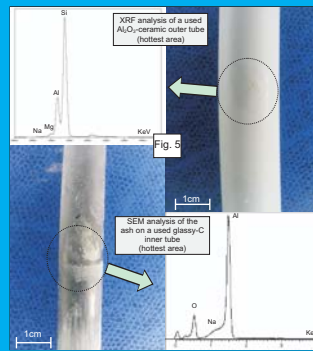


Fig. 5 - XRF analysis of a used  $\text{Al}_2\text{O}_3$ -ceramic outer tube (hottest area) and SEM analysis of the ash on a used glassy-C inner tube (hottest area).

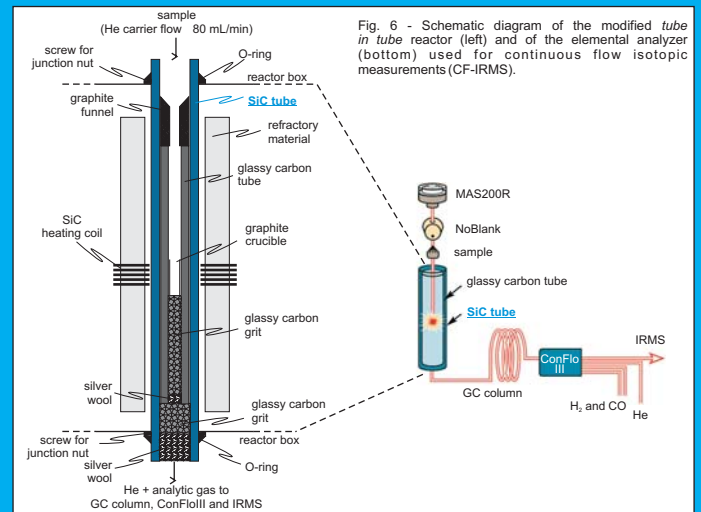


Fig. 6 - Schematic diagram of the modified tube in tube reactor (left) and of the elemental analyzer (bottom) used for continuous flow isotopic measurements (CF-IRMS).

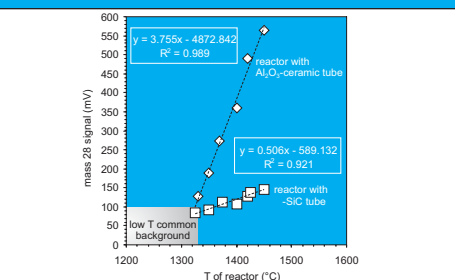


Fig. 7 - Signal on mass 28 ( $^{13}\text{C}^{18}\text{O}$ ) vs. temperature of the reactor. Open diamonds: signal with the  $\text{Al}_2\text{O}_3$ -ceramic reactor's tube; open squares: signal with the  $-\text{SiC}$ -reactor's tube. Least-squares regression lines of the data are also showed. Grey area depicts the usual background at  $T < 1325^\circ\text{C}$ .

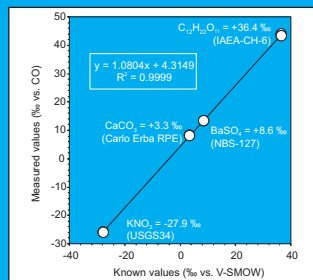


Fig. 8 - Calibration determined using various solid standard compounds. SiC-reactor and NoBlank autosampler device. For laboratory carbonate and *intercomparison* sulfate standards,  $\text{AgCH}_3\text{C}$  catalyst was used (Boschetti and Iacumin, 2005).

## Conclusion

The Thermo NoBlank sampling device, also compatible with other elemental analyzer brands, introduces: 1) an innovative technique for the solid sample introduction exploiting the time of previous analysis for the purging; 2) requires only 30 mL/min of He purge flow instead of 100 mL/min previously required; 3) a "ready to use" solution because no pre-analytic time is required for conditioning or after carousel addition. The reactor assembled with a high purity SiC outer tube allows to an effective background lowering on the CO masses and a longer life than ceramic reactor. The use of the NoBlank device coupled with the new SiC reactor's tube guarantee a stable baseline during the oxygen CR-CF-IRMS analysis of solid samples, the former preventing perturbations due to the air contamination, the latter improving the signal to background ratio.

## Acknowledgements

We are grateful to Guido Giuzzi, Liliana Krotz, Martino Villa (Thermo Electron Co. Milano - Italy) for their OEA support and Guglielmo Spadavecchia and Mirko Gianesella (Thermo Electron Co., Milano - Italy) for the XRay-analyses. Many thanks are owed to Antonio Longinelli (University of Parma, Italy) for valuable advice.

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