

UNDERSTANDING DETECTION LIMITS IN FLUID INCLUSION ANALYSIS USING AN INCREMENTAL CRUSH FAST SCAN METHOD FOR PLANETARY SCIENCE. N.J.F Blamey^{1,2}, J. Parnell², and H.P. Longrich³. ¹Department of Earth & Environmental Science, New Mexico Tech, Socorro, NM 87801, USA. ²School of Geosciences, University of Aberdeen, Aberdeen AB24 3UE, Scotland, UK. ³Department Earth Sciences, Memorial University of Newfoundland, St. John's, NL, A1B 3X5, Canada.

Introduction: Analysis of volatile components in fluid inclusion is not a new concept and analysis using mass spectrometry has been used for more than three decades. However it remains a rarely used procedure primarily due to the lack of geochemists who understand the intricacies and have the equipment to carry out this type of analysis. At New Mexico Tech there is a dual quadrupole mass spectrometer dedicated to the quantitative analysis of aqueous-dominated fluid inclusions using an incremental crush fast scan method [1, 2] as well as by bulk thermal decrepitation or crush with cryogenic separation [3].

Typically 200 mg of sample is cleaned with KOH, rinsed with deionised water, and then air dried prior to loading inside the crushing chamber. The sample chamber is evacuated to a vacuum of $\sim 10^{-8}$ Torr, and the sample is then incrementally crushed. The released gases (H_2 , He, CH_4 , H_2O , N_2 , H_2S , O_2 , Ar, CO_2 , SO_2 , C_2 - C_4 alkanes and benzene) remain in the chamber for 8-10 analyser scans of the quadrupole mass spectrometer which measures the gas-burst analyte signal (approximately 1 sec total) before being removed from the mass spectrometer chamber. This method is referred to as the incremental crush fast scan method [1, 2]. The data collected by the mass spectrometers is processed using proprietary software and the analysis for each burst is reported in mol percent. Most natural materials have an inherent variability hence several prepared microcapsules of air were analysed to estimate precision. For the encapsulated air the mean N_2/Ar ratio was 84.3 and the one sigma error was 0.4, or the relative standard deviation (RSD) was 0.5% for this synthetic standard. Earlier reports of the detection limits for aqueous fluid inclusion gases (such as Helium) were estimated at <0.5 ppm, the exception being H_2 for which the detection limit was estimated at 50 ppm [1,2].

To date, estimation of detection limits has been difficult to calculate for fluid inclusion gas analysis due to the transient nature of the sampling. However, this valuable figure of merit data is important for future analytical work where smaller samples are analysed to separate multiple fluid inclusion assemblages or to analyse scarce samples or where minute sample is available. This will become increasingly important in the analysis of samples for planetary science, including meteorite and

micrometeorite samples, and potentially from sample return missions. Previously detection limit calculations for LA-ICP-MS has been reported [4] and this approach is adaptable to quantitative fluid inclusion gas analysis due to the similar transient signals of both acquisitions.

For some analytes (such as CO_2) in fluid inclusions, the signals are 1-3 orders of magnitude above background, and thus knowledge of the detection limit is of little importance, however, for species such as CH_4 , He, and Ar which often have concentrations which are very low, in the ppm range, knowledge of the detection limit is important. Quantifying the detection limits is valuable, especially when these species are reported in discrimination diagrams used to recognise fluid sources [5].

The standard deviation of an individual determination of the background of a sample is given by the formula:

$$\sigma_{\text{individual}} = \sqrt{\frac{\sum(\bar{X} - X_i)^2}{n_b - 1}}$$

Longrich *et al.* [4] recognised for a Laser Ablation Inductively Coupled Plasma MS transient sampling signal that the measurement error included both elements of the background (n_b is number of cycles obtained from the background) and the analyte (n_a is number of cycles used for the measurement of the analyte signal) where the error associated with the net (analyte minus background) signal (σ_{Rnet}) equals the 1σ from the background times the square root of $1/n_b$ plus $1/n_a$ as shown in the formula below. Increasing either/or n_b or n_a will improve the limit of detection (LOD). For σ_{Rnet} , the standard deviation of the mean net signal (gross - background), both n_b and n_a are 10 thus improving the σ_{Rnet} by 0.45 times the $\sigma_{\text{individual}}$. Increasing acquisitions for either the background or analyte will improve estimates of the error, and LOD.

$$\sigma_{\text{Rnet}} = \sigma_{\text{individual}} \sqrt{\frac{1}{n_b} + \frac{1}{n_a}}$$

The term σ_{Rnet} is the standard deviation of the mean net signal and while it is common practise by geochemists to make 2σ as the confidence limits or approximately a 95% confidence limit. However for detection limits, usually a 99% or $\sim 3\sigma$ value is used to confirm that the analyte contains more than zero concentration. As the above standard deviation is in terms of signal count rates or other convenient units, it is more useful to convert this value to concentration units by dividing by the sensitivity, S (signal per unit concentration):

$$\text{LOD} = \frac{3\sigma_{\text{Rnet}}}{S}$$

As an example, several analyses from samples of an Ordovician pillow basalt sample (HB01) collected from Helen's Bay, Northern Ireland are shown in Table 1. Some gas concentrations greatly exceed the LOD by orders of magnitude such as methane whereas helium in crushes 8523a and 8523d is very close to the 3σ LOD. The analysis of basalt is important in the context of Martian exploration, as much of the surface of Mars is basaltic or andesitic. This sample has negligible water and only the major gas species are reported together with the LOD for each crush. The detection limit for aqueous-dominated inclusions would be suppressed due to the low water content. In this example, high levels of methane were determined in the basalt, which suggests that it would be very valuable to similarly analyse basaltic samples from Mars.

Two or three sigma may be statistically adequate to confirm the presence of gas concentrations close to the background but for presentation in discrimination

diagrams such as in Blamey [5] or Norman *et al.* [6], one may chose to use 10σ , in which case one would call it the Reporting Limit (LOR) if any value of n is used or conventionally the limit of quantitation (LOQ) when n equals 10.

$$\text{LOR} = \frac{10\sigma_{\text{Rnet}}}{S}$$

Conclusion: For gas analysis by the incremental crush fast-scan method we propose formulas for determination of the detection and reporting limits adapted from LA-ICP-MS formulae by Longerich *et al.* [4]. Either a 2 or 3 σ confidence limits may be applied for confirming the presence of a gas species whereas for presentation in discrimination diagrams we propose a 10σ confidence limit, thus permitting confidence in where the sample plots within discrimination diagrams.

The determination of very low detection limits gives us confidence in the application of this technology to samples of limited size (few mg) that are available in planetary science studies.

References: [1] Norman D.I. & Blamey N.J.F. (2001) *ECROFI XVI*, 341-344. [2] Parry W.T. & Blamey N.J.F. (2010) *Chem. Geol.*, 278, 105-119. [3] Norman D.I. & Sawkins (1987) *Geochem. et Cosmo. Acta.*, 61, 1-10. [4] Longerich H.P. *et al.* (1996) *J. Analytical Atomic Spectrometry*, 11, 899-904. [5] Blamey N.J.F. (in review) *J. Geochemical Exploration*. [6] Norman D.I. *et al.* (2002) *27th Workshop Geothermal Reservoir Engineering*, 266-274.

Crush #	H ₂	He	CH ₄	N ₂	H ₂ S	Ar	CO ₂
8523a	0.410 (0.0024)	0.0017 (0.0012)	45.09 (0.0017)	34.78 (0.019)	0.0053 (0.0054)	0.3923 (0.0020)	17.83 (0.021)
8523b	0.444 (0.0024)	0.0063 (0.0013)	46.61 (0.0016)	38.13 (0.023)	0.0456 (0.0029)	0.5474 (0.0034)	12.65 (0.037)
8523c	1.58 (0.0024)	0.0105 (0.0008)	51.95 (0.0020)	33.60 (0.031)	0.0706 (0.0032)	0.3671 (0.0022)	9.59 (0.037)
8523d	3.21 (0.0015)	0.0010 (0.0007)	49.47 (0.0010)	39.02 (0.014)	0.0249 (0.0017)	0.5053 (0.0016)	5.89 (0.023)

Table 1. Quantitative gas analyses performed on Helen's Bay basalt (HB01). Each analysis represents an incremental crush from which gases were released then analysed and reported in mol % together with corresponding detection limit (LOD) using 3σ (given in brackets). For most gases the signal is orders of magnitude above detection, however, for helium in crush 8523a the signal of 17 ppm is marginally above the 12 ppm LOD.