SHORT COMMUNICATION

Experimental Setup and Standardization of a Continuous Flow Stable Isotope Mass Spectrometer for Measuring Stable Isotopes of Carbon, Nitrogen and Sulfur in Environmental Samples

R. Agnihotri*, R. Kumar, M. V. S. N. Prasad, C. Sharma, S. K. Bhatia and B. C. Arya

Radio and Atmospheric Science Division, CSIR-National Physical Laboratory, New Delhi 110012, India

Abstract: We present here the experimental setup and standardization of a newly acquired stable isotope ratio mass-spectrometer (*Isoprime 100,* Isoprime® UK) coupled with elemental analyzer (*Pyrocube,* Elementar®-Germany) in a continuous flow mode, for the measurements of C, N and S isotopes in a variety of natural as well as synthetic organics and sulfur containing solid samples. We have calibrated our instrument using a suite of certified international standards supplied by *International Atomic Energy Agency Vienna* and cross-checked against several *in-house* laboratory standards used by other institutions of international repute. A synthetic organic compound *Sulfanilamide* was continuously used along with international standards to develop an *in-house* internal laboratory standard for the accurate and precise isotopic measurements. Important components contributing to the overall uncertainty of the isotopic measurements such as blank contributions, amount effect and response of mass-spectrometric current against thermal conductivity detector were performed using several aliquots of ε-Amino-*n*-caproic acid and *sulfanilamide* (*in-house*) standards. Both short and long term variabilities in the measure isotopic data were assessed using our *in-house* laboratory standard *Sulfanilamide.* Overall estimated uncertainties of C, N and S isotopic measurements are better than 0.2, 0.2 and 0.3 ‰, respectively; which are well within the recommended limits of aforementioned isotopic data.

1. Introduction

The Radio and Atmospheric Science Division of CSIR-National Physical Laboratory (CSIR-NPL, New Delhi) is engaged in monitoring various atmospheric parameters over different regions of northern India, especially focusing on physical, chemical and isotopic characterization of atmospheric aerosols and trace gases [1]. Towards achieving this goal, the division acquired a new 'state of the art' continuous flow isotope ratio mass-spectrometer (CF-IRMS) for measuring stable isotopes of carbon, nitrogen, sulfur, hydrogen and oxygen (C, N, S, H & O) in a variety of natural (environmental) as well as synthetic samples. This paper presents an overview of the experimental setup and standardization of the aforementioned CF-IRMS. In the concurrent environmental research of the lower troposphere, the aforementioned stable isotopes are

vital tools for (i) identification of source of organic and sulfur containing biomass material derived aerosols and trace gases (ii) understanding and quantifying degree of secondary transformations occurring within the atmosphere (aerosol secondary processes especially involving N cycling) (iii) evaluating net impacts on regional C, N and S biogeochemical cycles [2–5]. Stable isotopes of C and N in conjunction with other chemical parameters have proven their potential in deciphering as well as quantifying complex biogeochemical changes occurring on variety of timescales ranging from seasonal to millennial, in various earth system research fields viz. oceanography and limnology [6–12]. In addition, C and N isotopes have been successfully exploited as tracers of various emissions in the atmospheric aerosol sciences [13–16]. With modern developments in analytical methods in mass-spectrometry it has been demonstrated that S isotope ($\delta^{34}S$) can also be measured in small amounts of sulfur together with C and N isotopes in a sample aliquot with high sample throughput without compromising accuracy and precision [17]. As

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*Corresponding author, E-mail: agnir@nplindia.org

sulfate constitutes an important fraction of aerosol mass in both natural and anthropogenic emissions; S isotope of aerosol sulfur can be used for source apportionment [18]. Hence measuring a combination of C, N and S isotopes together with their concentrations can provide valuable inputs in the environmental research. In dealing with environmental samples (e.g. atmospheric aerosols), accurate and precise measurements of all the three N, C and S isotopes in same sample aliquot becomes more challenging as there could be significant variations in their relative amounts (such as C/N ratios of atmospheric aerosols could vary from ∼1 to 50 (e.g. [13]); in contrast to oceanic sediments where C/N ratios generally vary between ∼6 and 15 (e.g. [19]), requiring an optimal adjustment of various operating parameters. In addition to aforesaid stoichiometric difference, carbonaceous components may be differ widely in aerosols over varying environments in terms of their organic constituents (e.g. [20]). Therefore we carried out a detailed investigation on reliability (accuracy) and reproducibility of each isotopic measurement especially for sample containing low N or S contents (<2 μmol). While $\delta^{13}C$ and $\delta^{34}S$ isotopic measurements showed no observable amount or size effect for samples containing lower amounts of C and S (from 1 to 4 μmol), we observed there is a significant size or amount effect on $\delta^{15}N$ measurements especially for samples containing low N (<2 μmol of N). Through applying a proper blank correction, accurate and precise $\delta^{15}N$ data can be generated for variety of environmental samples.

2. Experimental Setup

Hence, to develop a multi-isotope measurement capability for variety of environmental samples (e.g. atmospheric aerosols, soil and dust samples), RASD of CSIR-NPL procured a new isotope ratio mass-spectrometer (Isoprime 100, *Isoprime UK*®; simply IRMS henceforth) coupled with an elemental analyzer (Pyrocube, Elementar®; EA henceforth). In recent years, several CF-IRMS's have been established in other institutions of India like National Institute of Oceanography (Goa and Vishakhapatnam), Physical Research Laboratory (Ahmedabad), Wadia Institute of Himalayan Geology (Dehradun) and Indian Institute of Technology (Kharagpur) for measuring light stable isotopes (C, N, S, H &O) in solids as well as in analytes dissolved in aqueous media. RASD's newly established CF-IRMS is relatively a bit advanced, as it is designed for simultaneous measurement of C, N, S isotopes in single aliquot of a natural/synthetic sample via flash-combustion pathway and H & O isotopic analysis via pyrolysis pathway.

Figure 1 shows the picture of NPL's newly established CF-IRMS. The two units are connected through continuous flow mode (open split device in a Helium environment). The *IsoPrime100* is the latest 'state of the art' gas source stable isotope ratio mass spectrometer, which has a completely redesigned 100 V head-amplifier, offering a wide dynamic range as well as automatic gain-switching, necessary for multi-isotopic measurements in same aliquot of sample. Enhancements in the ionization source are expected to result in better instrument performance with high sensitivity, precision and accuracy. The *IsoPrime100* offers determination of $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$ and δD, $\delta^{18}O$ via continuous flow mode connection with a EA (Pyrocube) through flash-combustion (combustion in presence of pure O_2) and pyrolysis (combustion without O_2), respectively. Sample introduction system is fully automated through *IonVantage* software to give excellent control and switching between inlet systems and gas species. Universal three cup collectors are used to collect the ion beams of C, N, O, S isotopes, and for H isotopes (δD) additional cup collector is provided. Analyte gas mixture (N_2, CO_2, and SO_2) is separated using *Purge & Trap* separation controlled by thermal programmed desorption (Fig. 2). *Purge & Trap* separation offers multi-elemental isotopic analyses with suitable baseline resolution. *Pyrocube* EA has *zero-blank* ball-valve technology for sample introduction. Each sample is individually purged before analysis resulting in reliable analysis of very low nitrogen concentrations. EA's sample carousel has 120 sample positions. All the daily maintenances can be done without usage of any tools due to ball and clamp fittings. Ash finger and furnace tube exchange can be done easily depending on requirement. Automated, leak checks can be performed via software controlled leak diagnostics program. Basic schematic of *Isoprime 100* mass-spectrometer coupled with EA in continuous flow mode is shown in the Fig. 2.

3. Theoretical Description of Notations Used in the Stable Isotopic Data

Isotopic anomalies are expressed in terms of ratio of less abundant (heavier) atoms with respect to naturally more abundant (lighter) atoms and they are expressed using Delta (δ) notation. For example, isotopes anomalies of carbon, nitrogen and sulfur are expressed as $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ respectively and defined as -

$$\delta = \left[\left(R_{\text{sample}} / R_{\text{standard}} \right) - 1 \right] \times 1000 \qquad (1)$$

where $R = {}^{13}C/{}^{12}C$, ${}^{15}N/{}^{14}N$ and ${}^{34}S/{}^{32}S$

Hence δ values are simply ratios expressed in per thousand (commonly known as per mil denoted by ‰). $\delta^{13}C$ values of all the carbon containing substances are

Fig. 1 A picture of NPL's CF-IRMS installed in the TEC building (room no. 108)
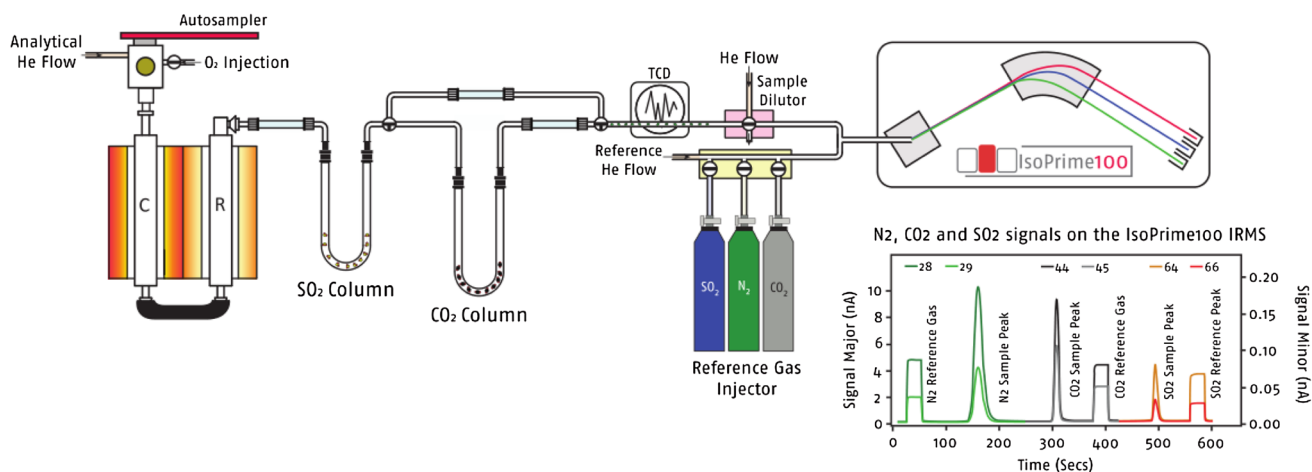

Fig. 2 Basic schematic of NPL-CFIRMS interfaced with EA in continuous flow mode. (source: isoprime technical note)

expressed with respect to Vienna-Peedee Belemnite (*V-PDB*). Likewise, $\delta^{15}N$ values are expressed with respect to atmospheric N_2, which is assumed to be of 0 ‰ value. The international standard for Sulfur isotope measurements is vienna-cation diablo troilite [18].

3.1. Sample Preparation and Methodology

To measure $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$ and their respective concentrations [total carbon (TC), total nitrogen (TN) and total sulfur (TS)] of solid environmental samples (e.g. soil, sediment, dust or atmospheric aerosols), suitable amount of sample is dried in oven (at ~ 60 °C), cooled in desiccators, weighed in appropriate amounts and packed in tin cups before introducing to EA's auto-sampler unit. In case of atmospheric aerosol samples collected on quartz filters, about 1–3 hole punches (area ~ 1 cm^2) of aerosol containing filters are cut and packed in suitable sized tin cups. It is important to use dried samples before weighing them in tin cups. Sediment samples can be dried in oven ~ 60 °C or freeze dried samples can also be used. Aerosol sample

are better to dry in desiccator only. Then round pellets should be made by pressing from all the sides to remove any air. Pellets have to be round or oval shaped to ensure their proper dropping into combustion tube. Number of filter punches or amounts of solid samples (e.g. soil or dust) taken for isotopic analysis is decided by a priori knowledge of expected C, N, and S contents. Generally solid samples can be weighed in the range of ~ 2–50 mg, where number of filter punches can be taken from 1 to 3. Packed tin cups are dropped into the combustion tube (heated at 1,120 °C) of the Pyrocube EA. The combustion tube is filled with tungsten oxide (WO_3) (padded with corundum balls and quartz wool) which acts as catalyst for the CNS mode. For only C and N isotopic determination a different filling can be used which contains copper oxide (CuO) and lead chromate ($PbCrO_4$) [21]. Flash combustion takes place in the presence of high purity (6-grade) oxygen gas (O_2). The evolved gases are passed through reduction tube (at 670 °C for CN mode and 850 °C for CNS mode) filled with activated metallic copper that reduces the oxides of nitrogen (NO_x) to N_2. Ensuring proper removal of NO_x is very

important for reliable isotopic data of N isotopes and also for S isotopes. That is why, for CNS mode temperature of the reduction tube is kept higher than that of CN mode. Dry helium (5.5 grade) is used as carrier gas for sample introduction. Gas streams are then passed through a water-trap filled with sicapent or magnesium perchlorate (MgClO4) ensuring complete removal of moisture. Sample N_2 is passed through directly to open split orifice of IRMS, while and CO_2 and SO_2 are held on two special CO_2 and SO_2 columns normally kept at temperatures 20–25 °C (room temperature) and 55 °C respectively. When N_2 analysis is over, CO_2 is allowed to be desorbed from CO_2 column by raising the temperature to 240 °C; similarly after CO_2 analysis, SO_2 is allowed to be desorbed from SO_2 column by raising the temperature to 220 °C. The typical chromatogram of simultaneous analysis of CNS isotopes using a *sulfanilamide* is shown in Fig. 3.

4. Background, Internal Stability and Linearity of the IRMS System

4.1. Background

Background in the CF-IRMS is mainly dependent on quality (purity level) of carrier gas (i.e. He gas and moisture levels present in Helium tank. High backgrounds may impair measurement inaccuracy and poor precision. In practice, these back ground values will vary from lab to lab, depending on the instrument configuration, the grade of gases used and many other factors. In general, it is recommended to use grade 5.5 (99.9995) He as a carrier gas in CF-IRMS. We show here a typical and ideal background scan of our CF-IRMS in Fig. 4. The observed background level for the water (moisture) is 0.12×10^{-10} A which is less than the maximum permissible background level (as recommended in the

Fig. 3 Typical chromatogram of a 'Sulfanilamide standard' run on NPL-CFIRMS. Time in seconds

Isoprime 100 manual) for water (moisture) i.e. 5×10^{-10} A. Similarly the observed background level for the N_2 0.108×10^{-10} A, which is less than the maximum permissible background level for N_2 i.e. 1×10^{-10} A. The Ar and CO_2 levels are significantly lower than their respective permissible levels described in the *Isoprime 100* manual which are $>1 \times 10^{-11}$ A for Ar and $>5 \times 10^{-11}$ A for CO_2. Background levels may not significantly affect reference gas stabilities, but may give rise to non-linearity effects and may eventually lead higher analytical uncertainties.

4.2. Reference Gas Stability Tests

It is important to monitor the stability of the measurement of the isotopic composition of the working gas on the daily basis. The stability of internal continuous flow system is determined using ten (or more) injections of each analyte gas (e.g. N_2, CO_2 and SO_2) at same pressure level (controlled by mass-flow controllers in the reference gas box) and isotopic abundances are measured. This set of measurements is also known as 'zero enrichment' or 'on–off' test. The standard deviation (SD) of these ten measurements are checked; if the analyte reference gases are properly tuned a priori, in general SDs for all the reference gases must be within 0.1 % for ensuring good (reproducible) isotopic measurements (Isoprime 100 manual). Here we show typical stability test results of N_2, CO_2 and SO_2 that show typical SDs as 0.01, 0.01 and 0.07 % respectively (Fig. 5). Hence the actual stabilities achievable by NPL-IRMS are better than maximum permissible limits. Better tuning of reference gases and consistency of temperature and relative humidity conditions in the IRMS lab are key for achieving better stabilities and thereby more precise isotopic measurements.

4.3. Reference Gas Linearity Tests

Reference gas linearity test is conducted in same way as stability test except reference gas pressures are manually changed from mass-flow controllers of reference gas box. By changing the reference gas pressure, amount of analyte gas and hence IRMS current is varied and isotopic measurements are made. Measured isotopic values on varying IRMS current are checked for stability which should be within 0.1(‰/nA). This exercise is normally not done in routine running of CF-IRMS on daily basis, but has to be conducted and checked periodically. The intensity of working gas pulses must encompass the intensities of the sample to be determined, i.e. if sample are measured in the range 5,000–15,000 mV the linearity measurement should cover the range 4,000–16,000 mV. We have shown here typical linearity tests of N_2, CO_2 and SO_2 which are 0.01, 0.02 and 0.01 respectively, as shown in Fig. 6. It is
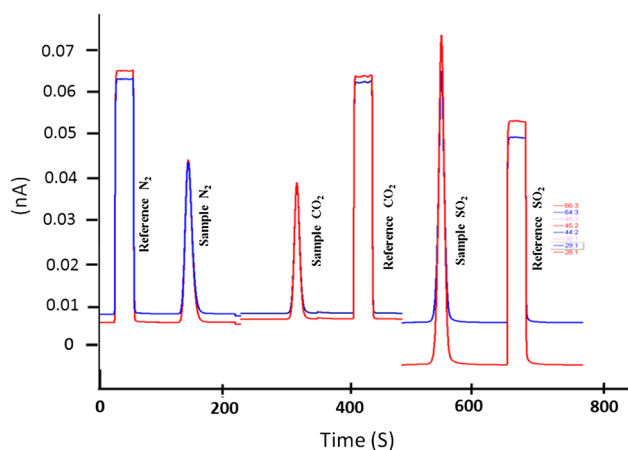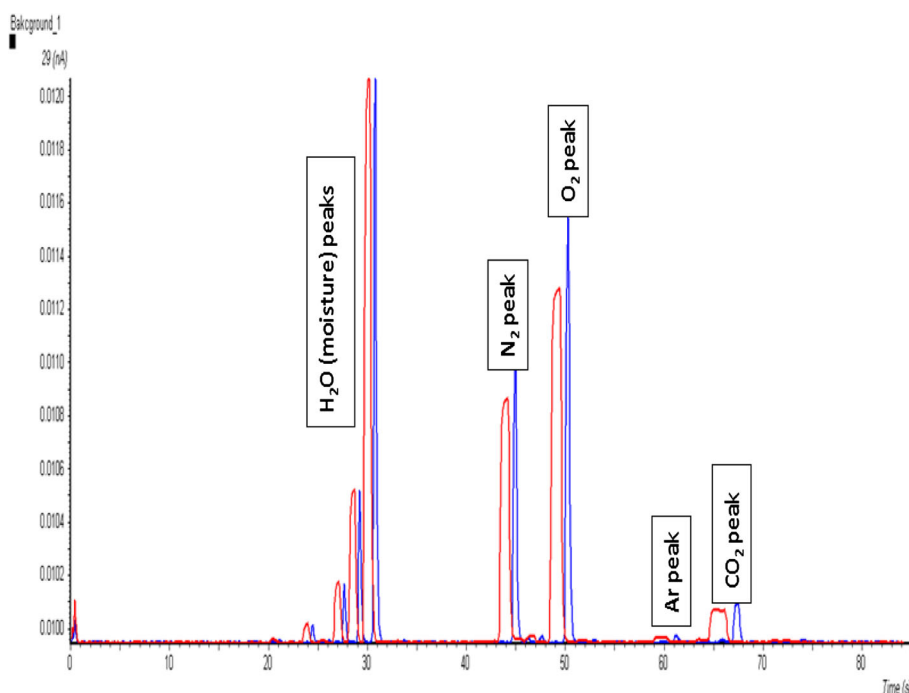
Fig. 4 A typical 'background' run measured on 12-09-2013

important to mention that linearity test in Isoprime mass-spectrometer is not automatic and gas pressures have to be altered manually. In the case of N_2 and CO_2, changing inlet gas pressure is relatively simpler to manage compared to the case of SO_2 where it is little bit more time taking and difficult to do in multiple steps as SO_2 pressure adjustment is not that easy manually.

4.4. Calibration of CNS Isotopic Data

The C and N mass concentrations and their isotopic measurements ($\delta^{15}N$, $\delta^{13}C$) of NPL-CFIRMS were mainly calibrated using an international standard i.e. ε-Amino-*n*-Caproic acid [$C_6H_{15}NO_2$] that is generally known as ACA, a laboratory standard used in School of Marine Science and Technology, University of Massachusetts USA. This standard was acquired through the good offices of Prof. Mark Altabet. Reported values of $\delta^{15}N$ and $\delta^{13}C$ are 4.6 and −25.3 ‰ respectively. Reference gas tanks were calibrated initially by running several aliquots of ACA and then offsets between actual isotopic values from those of measured values were estimated. The obtained offsets were incorporated in Ionvontage software of CF-IRMS to obtain calibrated isotopic values. We also used two other international standards viz. Japan-Glutamic acid (through the good offices of Dr. VVSS Sarma of NIO, Vishakhapatnam), IAEA-N-2 and IAEA-CH-6 for which reported (consensus) isotopic values are also known. We have shown plots of measured and calibrated values of $\delta^{15}N$ and $\delta^{13}C$ against respective reported values in Fig. 7. Likewise,

calibration of S content and $\delta^{34}S$ values was accomplished using three international IAEA standards (IAEA-S-1; IAEA-S-2 and IAEA-SO5; Fig. 7). The correlations (r^2 values) obtained for all the isotopic measurements are better than 0.9 (Fig. 7).

For developing an internal laboratory standard for CNS isotopic measurements, we used solid powdered Sulfanilamide ($C_6H_8N_2O_2S$). Contents of CNS are known for this standard but isotopic values were not known. A few aliquots of Sulfanilamide were always run in tandem with aforementioned international standards and standardized isotopic values were obtained. The calibrated isotopic values of $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ values are −1.03, −27.29 and 1.23 ‰ respectively. We have shown stability of nine *Sulfanilamide* runs made on single day in the (Fig. 8a).

4.5. Blank Determination

In the CNS isotopic analysis by CF-IRMS, it is important to ascertain blank levels. Procedure of blank determination is decided by type of sample. For example, in case of solid soil, sediment or dust samples, a few empty cleaned tin cups are just packed and run as samples. Whereas, for aerosol samples collected on quartz filers, same size aliquots of pre-combusted quartz filters are packed in clean cups and run as samples.

We always run a few (at least 2–3) pellets made with empty tin cups as blank in the beginning of analysis. Generally no detectable blanks are seen in the
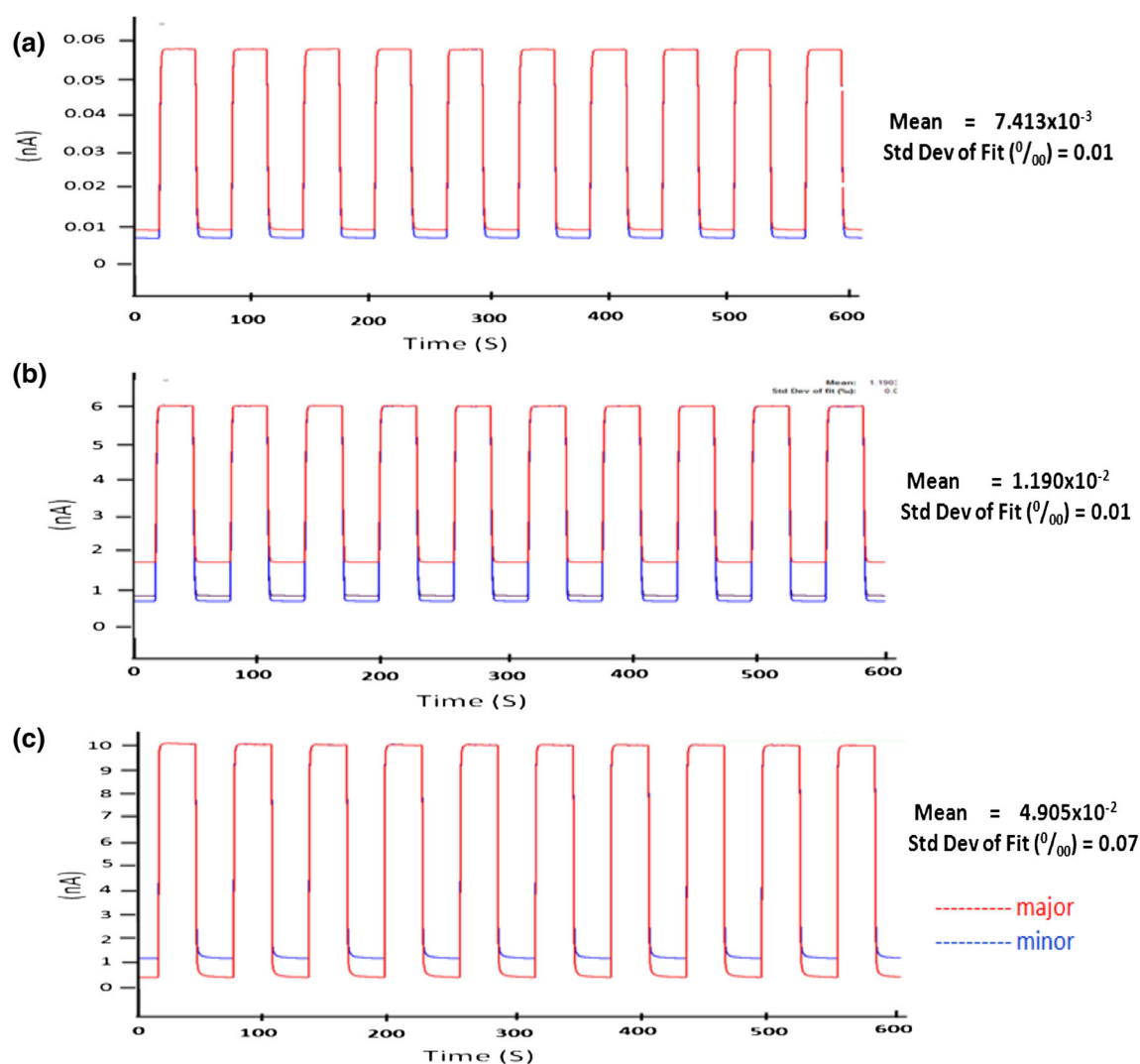
Fig. 5 Typical chromatogram of reference gas stability **a** N_2, **b** CO_2 and **c** SO_2

chromatogram for the empty tin cups, nonetheless, CNS areas measured on TCD of *Pyrocube* EA are corrected by mean values of at least two blank runs. For analysis of aerosol samples, field blanks of quartz filters are also cut into same size of hole-punches ($\phi = 1$ cm) and packed in tin cup to make pellets. These pellets are run in similar way as samples. Important to note that, blank levels are significantly influenced by purity levels of He and O_2 used for isotopic analysis. Blank filter aliquots often show detectable peaks on TCD which are equivalent to ~ 0.02 and 0.11 μmol of N, 0.2–0.6 μmol of C, and 0.06–0.11 μmol of S, which are generally at least 10–12 times smaller than the minimum analyte signals of CNS typically measured. Therefore we did make blank corrections for estimating final TN, TC, TS mass concentrations using mean blank filter values. We carried out blank correction for $\delta^{15}N$ measurements especially samples containing N < 2 μmol

(described in detail in the Sect. 9; amount effect). For the isotopic data of $\delta^{13}C$ and $\delta^{34}S$, however, we have not made any blank correction.

4.6. Long Term Reproducibility of the Instrument

For the long term stability of isotopic measurements we show here the results of in-house laboratory standard (Sulfanilamide) as several aliquots of it were always run along with all types of samples. Figure 8b shows average values of $\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$ obtained on each day of instrument run along with respective ranges (shown as uncertainty bars) and their long term means. Presented data do not show any evidence of a systematic drift or trend and overall uncertainties (1σ standard deviations) are well within reportable uncertainties on the isotopic measurements (*i.e.* 0.2–0.3 ‰).

Fig. 6 Typical chromatograms of linearity **a** for N_2, **b** for CO_2 and **c** for SO_2. Linearity was conducted by varying inlet pressures of analyte gases from 8 to 20 psi. For N_2 and CO_2 pressures were increased at smaller steps, inlet pressure could only be increase at two steps in case of SO_2
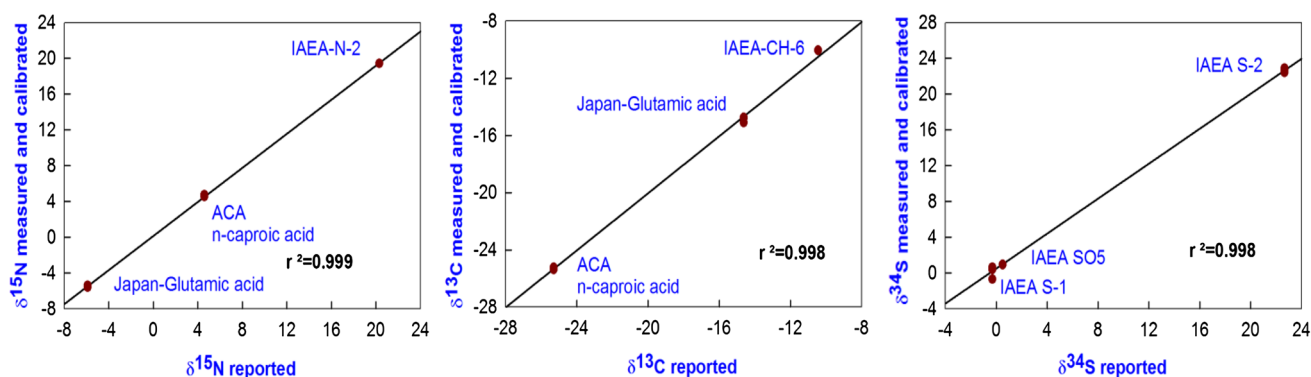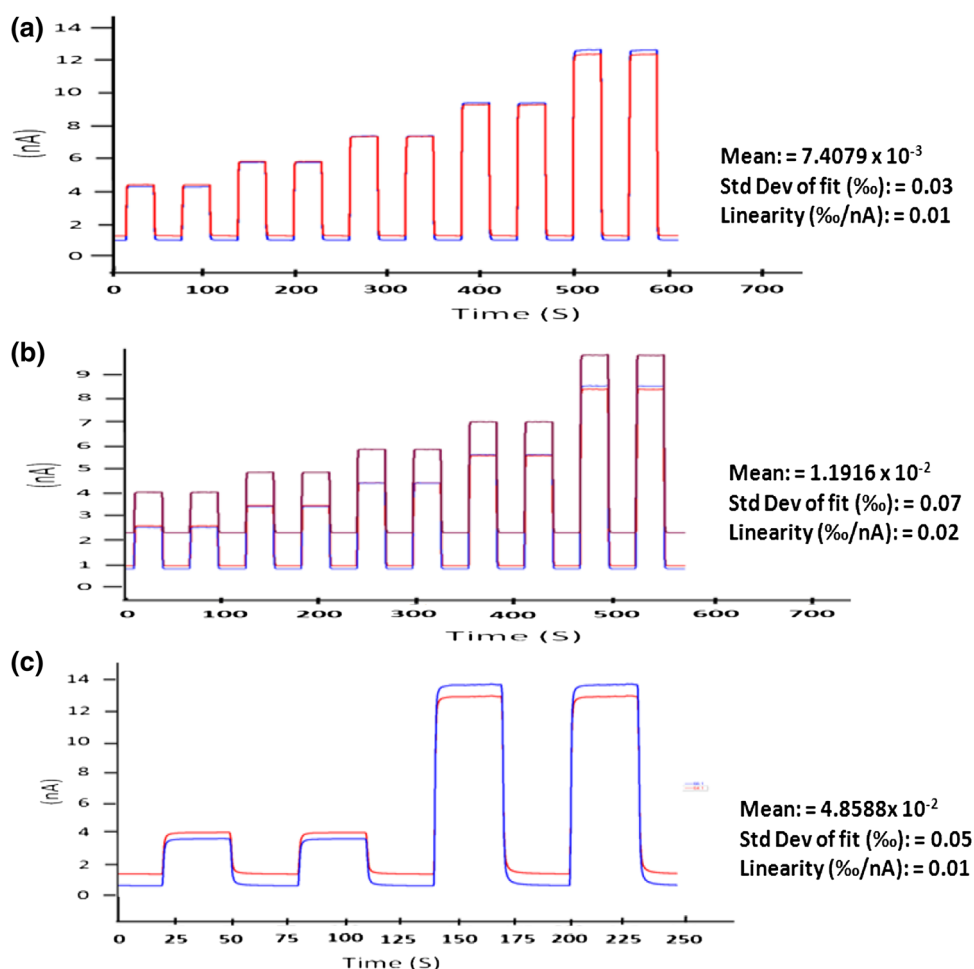

(a)

Mean: = 7.4079×10^{-3}
Std Dev of fit (‰): = 0.03
Linearity (‰/nA): = 0.01

(b)

Mean: = 1.1916×10^{-2}
Std Dev of fit (‰): = 0.07
Linearity (‰/nA): = 0.02

(c)

Mean: = 4.8588×10^{-2}
Std Dev of fit (‰): = 0.05
Linearity (‰/nA): = 0.01

Fig. 7 Calibration of CNS isotopic measurements against international standard results for accuracy

4.7. Effect of Amount on CNS Isotopic Measurements

Amount or size effect on N isotope measurements is known to be significant especially in samples having lower amount of N [22, 23]. The reason for this is (i) in general, the amount of N in natural samples is much lesser (~ 7–50 times) than that of C content and (ii) He tanks used for supplying pure He as carrier gas are prone to have some background levels of N_2. Therefore it is necessary to understand and correct for size effect on N isotopic measurements to achieve better accuracy. As it is little difficult to make standards containing low N (<2 µmol) gravimetrically, we used dissolved ACA solution to obtain N standards containing 0.5, 1, 2 and 4 µmol of N. For this known weight of solid ACA was dissolved in known volume of deionized water in such a way that 100 µl of the solution contains 4 µmol of N and 24 µmol of C. Then 100, 50, 25 and 12.5 µl volumes of the dissolved ACA solution
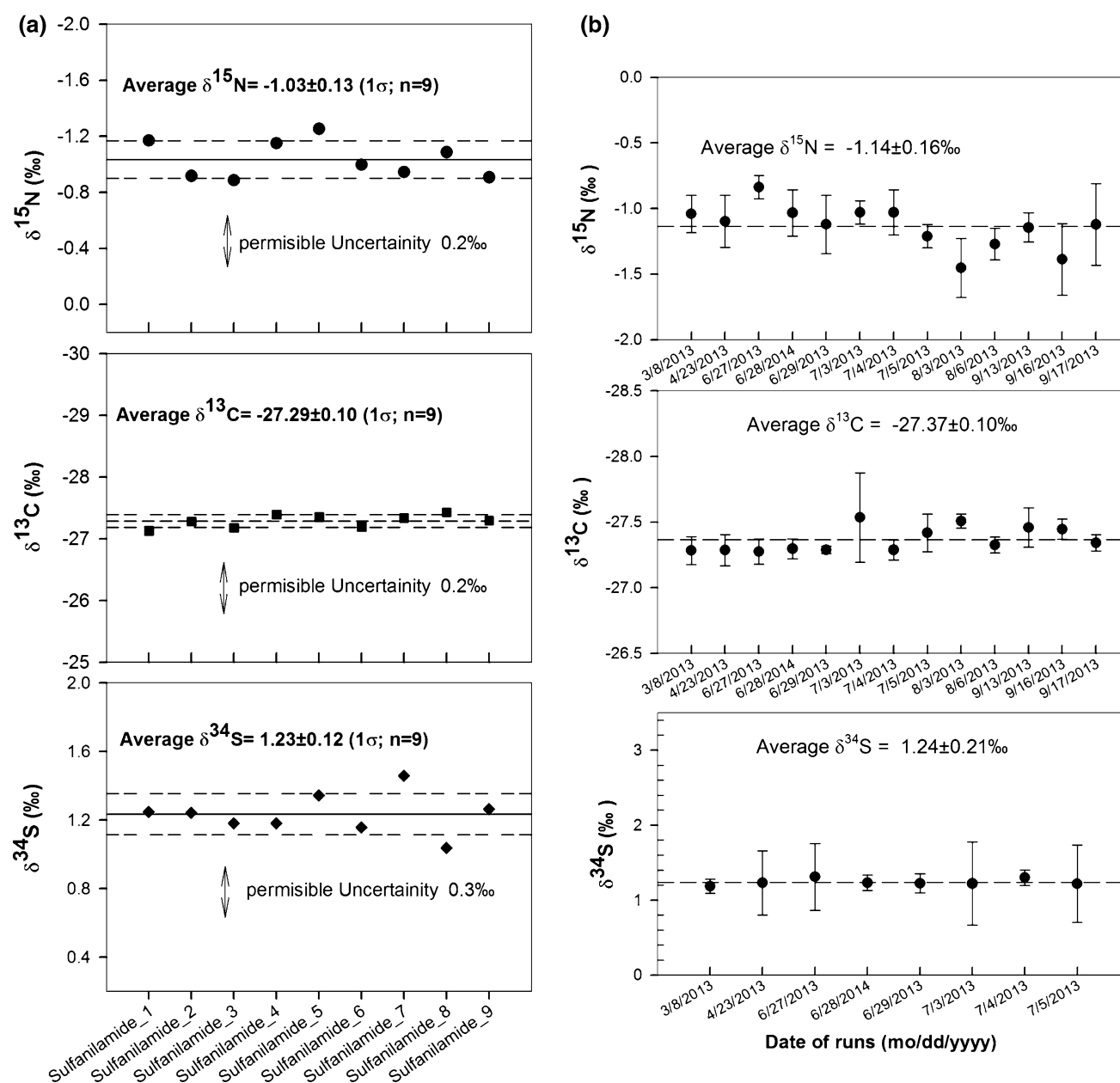
Fig. 8 **a** Depiction of reproducibility achieved by running different aliquots of internal laboratory standard Sulfanilamide made on single day. **b** Stability of isotopic values measured by sulfanilamide runs ($\sim$3–8 aliquots were run on each day of analysis) on different days from March–September 2013

were pipetted on pre-combusted quartz (or GF/F) filter punches (of diameter $\sim$1 cm) and left for overnight evaporation. Next day dried filter papers containing different amounts of N and C were packed in circular pre-cleaned Tin cups and transformed into pellets. Amount or size effects on C, N isotopic measurements were estimated by running these dried ACAs which correspond to 0.5, 1.0, 2.0 and 4.0 μmol of N and 3, 6, 12 and 24 μmol of C. Figure 9 shows the obtained results. As can be seen lower amounts of N tend to overestimate δ^{15}N significantly. It

was decided to carry out blank correction using following equation.

$$\delta^{15}N_{corrected} = \big[\{\big(\delta^{15}N_{sample} \times nA_{sample}\big) \\ -(nA_{blank} \times \delta^{15}N_{blank}\}/(nA_{sample} - nA_{blank})\big]$$

(2)

where nA stands for measured IRMS current for sample or blank. As $\delta^{15}N_{blank}$ could be highly variable (due to several factors like difficulties in integrating small peak, internal
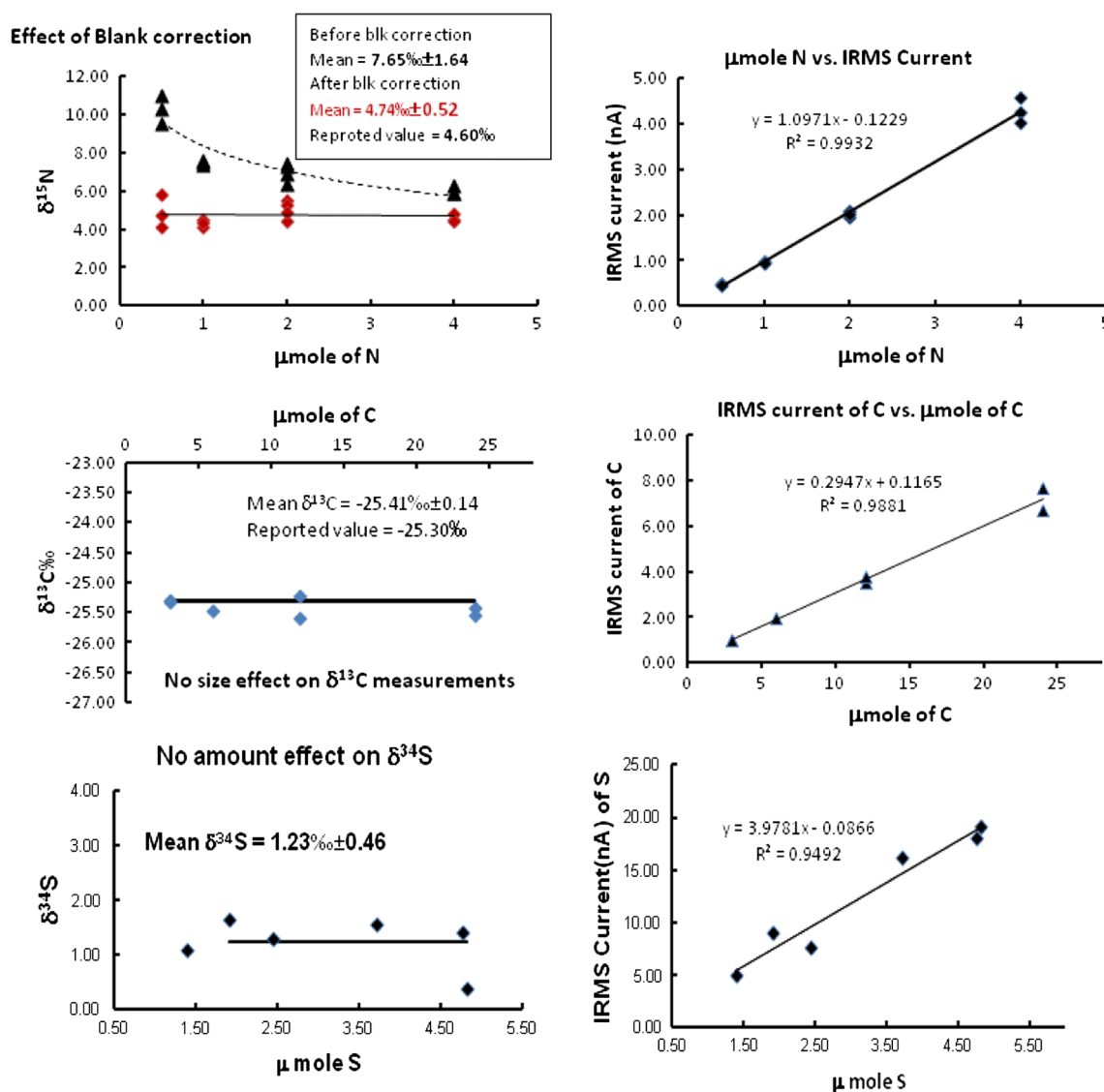
Fig. 9 a Amount or size effect on N, C and S isotopic measurements as measured by running several aliquots of ACA containing varying amounts of N and C and Sulfanilamide (for S isotopes). **b** Observed linearity of ISMR currents with respect to varying NCS contents

electronic noise etc.), it is estimated by plotting $\delta^{15}N$ of sample (ACA standards) against 1/nA (i.e. 1/respective IRMS currents). From the $\delta^{15}N-(1/nA)$ plot, slope and intercepts are evaluated. Then using the following formula $\delta^{15}N_{blank}$ is estimated

$$\delta^{15}N_{blank} = (Slope/nA_{blank}) + Intercept \qquad (3)$$

We have adopted this blank correction approach from Avak andFry [19, 23]. To get a realistic and effective correction on measured $\delta^{15}N$ it is very important (i) to run standards containing very low N contents (as low as possible) and (ii) to run several aliquots of blank comprising blank EA space, empty Tin foils and blank substrate (e.g. pre-combusted quartz filter punches). The average IRMS current corresponding to N blank is

0.07 nA. Figure 9a shows blank corrected $\delta^{15}N$ of *n*-caproic acid (ACA). Figure 9a also shows that there is no observable size effect on $\delta^{13}C$ and there are excellent proportionality between N and C contents and their corresponding IRMS currents.

Similarly size effect on $\delta^{34}S$ values was investigated using several aliquots of sulfanilamide (between 0.3 and 0.9 mg). Similar to the case for C, there is no observable size effect on $\delta^{34}S$ and there is an excellent proportionality between S contents and their corresponding IRMS currents. As it is difficult to go down with S content gravimetrically, to investigate any size effect on S isotopic measurement, similar to ACA solution we made ammonium sulfate solution in deionized water in such a way that we are able to get 100, 50 and 25 μl of solutions (through pipette) on

pre-combusted quartz filters corresponding to 4, 2 and 1 μmol of S respectively. Results of these aliquots on EA-IRMS are shown in Fig. 10. As can be seen from the Fig. 10, there is no apparent size or amount effect on the measured $\delta^{34}S$ and as expected there is an excellent proportionality between S content (in μmol) and corresponding IRMS current. We recommend here therefore, in case of only N isotopic measurements, blank correction are necessary especially for sample containing low N contents (<2 μmol of N i.e. ~20 μg of N).

We also checked the sensitivities of Pyrocube EA's thermal conductivity detector (TCD) and respective IRMS currents for all the three analytes gases N_2, CO_2 and SO_2. Figure 11 shows excellent 'proportionality' between the two detection techniques, hence any of them (or both) can be used for accurate and precise determination of elemental concentrations.

4.8. Concluding Remarks and Scope of Future Work

Thus, we show the experimental setup of a newly established CF-IRMS facility in RASD for isotopic measurements of C, N and S along with their concentrations in variety of natural (environmental) and synthetic carbonaceous and sulfur containing samples. Accuracies and precisions of the instrument were checked with several international and *in-house* isotopic standards. Generated data clearly shows overall reproducibility of C, N, S isotopic measurements are within to 0.2–0.3 ‰. In addition, on-line production of analyte gases viz. N_2, CO_2 and SO_2 by Purocube EA coupled with *Isoprime 100* IRMS in continuous flow mode is capable of yielding high sample throughput (~40–80 samples per day) without any significant drift. Long-term running of laboratory standard Sulfanilamide do not show any systematic trends and stability for all C, N and S isotopes is close to practical precision achievable on these isotopic data (0.2–0.3 ‰).

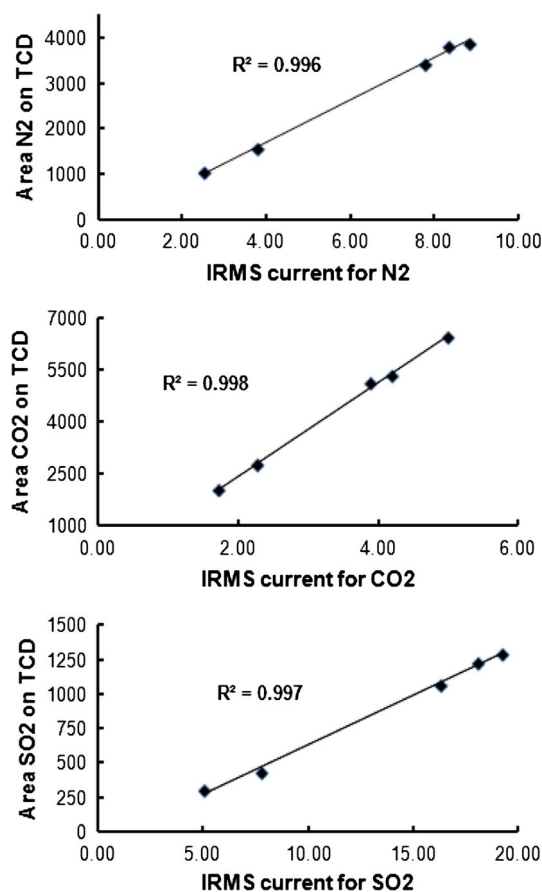Even though aforementioned blank correction appears to work for $\delta^{15}N$ measurements for better accuracy and

Fig. 11 Comparison of thermal conductivity detector (TCD) response against IRMS current for all three analytes gases N_2, CO_2 and SO_2. Plots show that variable of response of TCD is linear with respect to that of proportional IRMS current

precision, we believe better quality of Helium carrier gas and high purity O_2 can significantly reduce amount of blank. This will help for accurate and precise isotopic measurements of specific environmental samples containing very low amounts of N as may be the case for aerosols over polar or high altitude regions. Following aforementioned experimental protocol, N, C and S isotopic
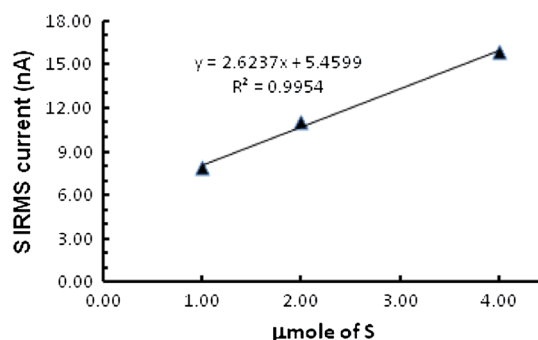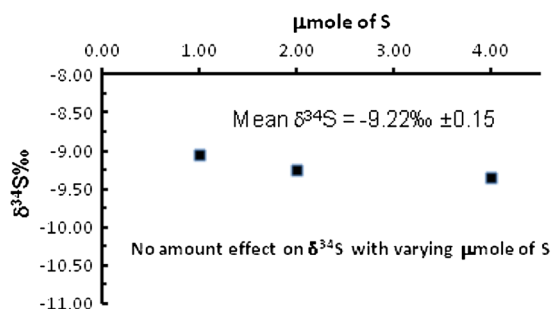
Fig. 10 Analysis of $(NH_4)_2SO_4$ solution (dried aliquots on pre-combusted filter punches) showing no size or amount effect on measurement of $\delta^{34}S$ and excellent proportionality between S content (in μmol) and corresponding IRMS current

measurements coupled with their concentrations can provide useful information in several atmospheric pollution studies and related ones (e.g. [24–26]).

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