21GRD04 isoMET

D2 - Guidelines on adapting optical isotope ratio measurements of ambient CH_4 to field conditions: Maintaining traceability of measurement and common practices for uncertainty calculation, including concept for harmonisation of CH_4 field site measurements

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1 Summary

This document contains guidelines on adapting optical isotope ratio measurements of ambient CH_4 to field conditions: Maintaining traceability of measurement and common practices for uncertainty calculation, including concept for harmonisation of CH_4 field site measurements.

2 Introduction

Accurate and reliable CH_4 isotope ratio measurements are required to pinpoint the sources of CH_4 in the atmosphere. To perform accurate measurements, accurate certified reference materials (CRM) for calibration of instruments are required to ensure traceability to international scales e.g. VPDB. Within the isoMET project, 35 CRMs were developed by NPL for calibration of partners' analysers. The aim of developing these new NMI-based CRMs was to bring together distinct CH_4 isotope measurement methods and allow a direct comparison of instrument performance and, to assess their suitability for CH_4 isotope ratio measurements. To assess suitability, standard operating and calibration procedures as well as common practices for uncertainty calculation for the OIRS instruments suitable for field site operation were developed. In addition, a metrological concept for harmonisation of CH_4 field site measurements, including gas sampling/treatment (e.g. flushing time) and sensor calibration/uncertainty calculations has been developed.

2.1 Adapting OIRS measurements of ambient CH_4 to field conditions

Adapting an OIRS instrument for field CH_4 measurements (i.e. an environment where external factors like temperature, humidity, pressure, and matrix gas composition are unstable and sometimes unknown) is a challenging task. The process begins in the laboratory with setting up a sampling system. The sampling system should ideally be the same as the system to be used at the field site. While measurements of isotopic CH_4 in air do not require any special coating for the components (e.g. tubing) of the sampling system, common good practices for sample system design such as minimizing the sampling volume and avoiding permeable rubber gaskets and plastic tubing should be followed. For more details on sampling procedures and sampling system design also see the deliverables D5 and D6 of the EMPIR project 19ENV05 STELLAR [1-2].

With the sampling system in place, the instrument is characterized and calibrated as described in deliverable five (D5) of the EMPIR project 19ENV05 STELLAR [2]. While D5 from STELLAR focuses on CO_2, the steps for the instrument characterisation can also be applied to CH_4 measurements. It should be noted that the common issue of fractionation is not a problem for CH_4 measurements in laboratory and field conditions.

The characterization steps are to determine, perform or evaluate:

1. Information about the instrument, data evaluation steps and the fitted spectrum
2. Limit of detection
3. Response of the instrument
4. Instrument stability
5. Calibration
    a. calibration approach
6. Amount fraction dependency of the isotope ratio
7. Matrix gas effects
8. Repeatability and reproducibility
9. Temperature effects

For a detailed description of step one to seven, see [2]. Regarding instrument calibration, different calibration approaches can be applied. Common calibration approaches are the isotope ratio (delta space) and the isotopologue (isotopologue space) based calibration approaches [2]. The isotope ratio calibration approach requires calibration with reference materials with different isotope ratios, the isotopologue based calibration approach requires calibration with well characterised amount fraction reference materials of one isotope ratio to determine the amount fraction of each isotopologue. The instrument operator can choose either of the calibration approaches if both are available on the analyser used and if the availability of CRMs allows it.
For a delta scale calibration, additional uncertainties could be added by e.g. the applied correction for matrix effects and concentration dependency on the measured isotope ratio. The characterization of the matrix gas effects described in step seven should consider the effects of:

- Ar range: from 0.5 to 1.5 %
- CO_2 range: from 0.03 to 0.05 %
- O_2 range: from 19 to 22 %.

Other matrix gases might also be of interest depending on the specific analyser and the expected conditions at the field site.

Step eight has been added to account for external (ambient) temperature effects on the instrument response (isotope ratio) during field measurements. The external temperature effect test could be performed by placing the instrument in e.g. a climate chamber and repeating a stability test while varying the temperature in the chamber. The generated temperature variations should cover the expected temperatures at the field site. A temperature coefficient (Δ‰/ΔT) is derived for data and uncertainty evaluation.

2.2 Maintaining traceability of measurement

Calibration procedures and strategies for $\delta^{13}C$ (CH_4) and δ^2H (CH_4) instruments, establishing traceability, have been discussed in literature [3-4]. Traceability should be maintained to the VPDB and VSMOW/SLAP scales. A calibration with two isotopic compositions at two concentration values chosen in a way that the expected measurement range with respect to the concentration and the isotopic composition is bracketed is generally seen as sufficient [3]. Further details on calibration methods can be found in [3]. The CRM used in this project were prepared by NPL and are traceable to the VPDB scales. The calibration interval is an important parameter that must be carefully chosen. For instruments like the Picarro G2201-I, the calibration interval recommended by the manufacturer is between three and four hours [6]. Evaluating the drift of the instrument is important to determine the calibration interval and maintaining traceability. The instrument drift can be determined by fitting a linear function to the measured data and evaluating the slope of the fit or by calculating the average of measurements over e.g. one-hour long intervals and subsequently evaluating the differences between the averages of the several intervals. Both methods can also be used to estimate the time an instrument will stay well within the target uncertainty of 0.2 ‰ for $\delta^{13}C$ (CH_4) and 2 ‰ for $\delta^2H(CH_4)$.

To maintain field data quality, the averaging time for the processing (or post processing) can be determined with an Allan variance analysis [2]. Preliminary tests of the Picarro G2201-i at PTB show that an averaging time of around 300 s is a practical choice. In addition to maintaining the data quality, it also necessary to check the measured data for errors. This is important to maintain traceability. Several simple checks (quality control/quality assurance: QC/QA) can be applied within the target measurement range, i.e.

1. low limit: check for $\delta^{13}C$ (CH_4) and $\delta^2H(CH_4)$ low values
2. high limit: check for $\delta^{13}C$ (CH_4) and $\delta^2H(CH_4)$ high values
3. data spikes: using e.g. a moving median filter, spikes in the measurements can be detected

In all cases the data flagged should be further checked by the experimentalist.

2.3 Common practices for uncertainty calculation

The process of uncertainty estimation for isotope ratio measurements including suitable model functions is described in detail in section 5 of D5 from the STELLAR project [2]. Table 1 shows the model function with the input parameters from [2] adapted for isotope ratio measurements in CH_4. The input data for the calculation of the measurement uncertainty is determined during the instrument characterization in the laboratory as well as during the field validations. The uncertainty of the CRM amount fraction is provided by the CRM manufacturer e.g. NPL as the CRMs in the isoMET project were mostly provided by NPL. It should be noted that the model function shown in Table 1 (in this case based on isotope ratio calibration approach) can only be directly applied if a two-point calibration is used. As mentioned, further details on calibration approached can be found in [3-4]. If more calibration points are used the slope m_{exp} and the intercept b_{exp} should be determined by fitting.

Used model function:

$$\delta_{cal} = m_{exp} \cdot \underbrace{(\delta_{raw} + \Delta\delta_c + \sum_{i=1}^{N} \Delta\delta_{m(i)} + \Delta\delta_D + \Delta\delta_T)}_{\delta_{raw,cor}} + b_{exp}$$

with $m_{exp} := \frac{\delta_{cal,2} - \delta_{cal,1}}{\delta_{raw,cor,2} - \delta_{raw,cor,1}}$ and $b_{exp} := \frac{\delta_{cal1}\delta_{raw,cor,2} - \delta_{cal2}\delta_{raw,cor,1}}{\delta_{raw,cor,2} - \delta_{raw,cor,1}}$

Operating conditions:
Cell pressure, flow rate, averaging time and fit settings need to be noted.

Input variable	Symbol	Unit	Standard uncertainty	Source of information	Type A/B
instrument realization of the measurand δ_{raw} (raw delta value)	δ_{raw}	‰	$\sigma^2(\overline{\delta_{raw}(t)}) = \frac{\sigma^2(\delta_{raw}(t))}{\sqrt{N}}$	instrument data	A
Concentration dependence	$\Delta\delta_c$	‰	$u(\Delta\delta_c)$	Determined from experiments on amount fraction dependency of the isotope ratio	B
matrix gas i effects (e.g., Ar, CO_2 or O_2)	$\Delta\delta_m = \sum_{i=1}^{N} \Delta\delta_{m(i)}$	‰	$\sum_{i=1}^{N} u(\Delta\delta_{m(i)})$	Determined from experiments on matrix gas effect on the isotope ratio	B
Instrument drift	δ_D	‰	$u(\delta_D)$	Determine from long term stability measurements	A
Temperature dependence effect	$\Delta\delta_T$	‰	$u(\Delta\delta_T)$	Determined from experiments on the effects on external temperature changes on the isotope ratio	B

Table 1: Model function and input parameters for the uncertainty estimation. Adapted from [2].

The amount fraction dependency of the isotope ratio and the influence of matrix gas on the isotope ratio can be described by appropriate functions determined via experiment on the change of the isotope ratio as a function of the change in the CH_4 concentration or matrix gas e.g. Ar. In the simplest case linear functions are sufficient to approximate the dependencies. More options for different function types are discussed in [2]. Note: It is important that the matrix gas composition of the CRM is well known to determine if matrix gas corrections are necessary. Further, it should be noted that a continuous correction of matrix gas effects is only possible if the matrix gases are measured continuously during operation. If this is not the case, the correction function should be replaced with a constant uncertainty that accounts for the effects of the matrix gas variations expected at the field site.

2.4 Concept for harmonisation of CH_4 field site measurements

The flowchart in Figure 1 outlines the proposed concept to harmonized CH_4 field site isotope ratio measurements. The process begins with the characterization and calibration of the instrument including the sampling system in the laboratory. As presented, more details on sampling procedures and sampling system design can be seen in D5 and D6 of the EMPIR project 19ENV05 STELLAR [1-2]. With the sampling system in place, the instrument is characterized and calibrated. The characterisation is done as described in section 2.1 and the calibration as described in section 2.2. The instrument characterization should follow a characterization protocol that includes the points listed in section 2.1 as well as using a working standard ("cheaper" gas compared to the CRM) to minimize the usage of the CRM. Once the characterisation of the instrument is completed, it can then be calibrated using available CRMs ("references"). Once the calibration is completed, a laboratory uncertainty is calculated (see Table 1). After this laboratory calibration in completed, the instrument can be deployed to the field site. At the field site, the instrument is then validated in fixed intervals using e.g. a working standards or CRM, depending on the availability of the CRM and the gas consumption. A working standard is recommended for the regular field validation to limit CRM gas consumption. The length of the interval and the extent of the validation depends on the results of the characterization of the instrument as described 2.1. After each field validation a quick QC/QA check should be performed to ensure that the instrument drift is within the expected levels. The check should be able to identify an instrument fault or a severe problem with the sampling system. Before the field data is passed on to the end user, it should undergo a final plausibility check (QC/QA) to prevent obvious incorrect data from being published. Types of possible QC/QA checks are listed in section 2.2.

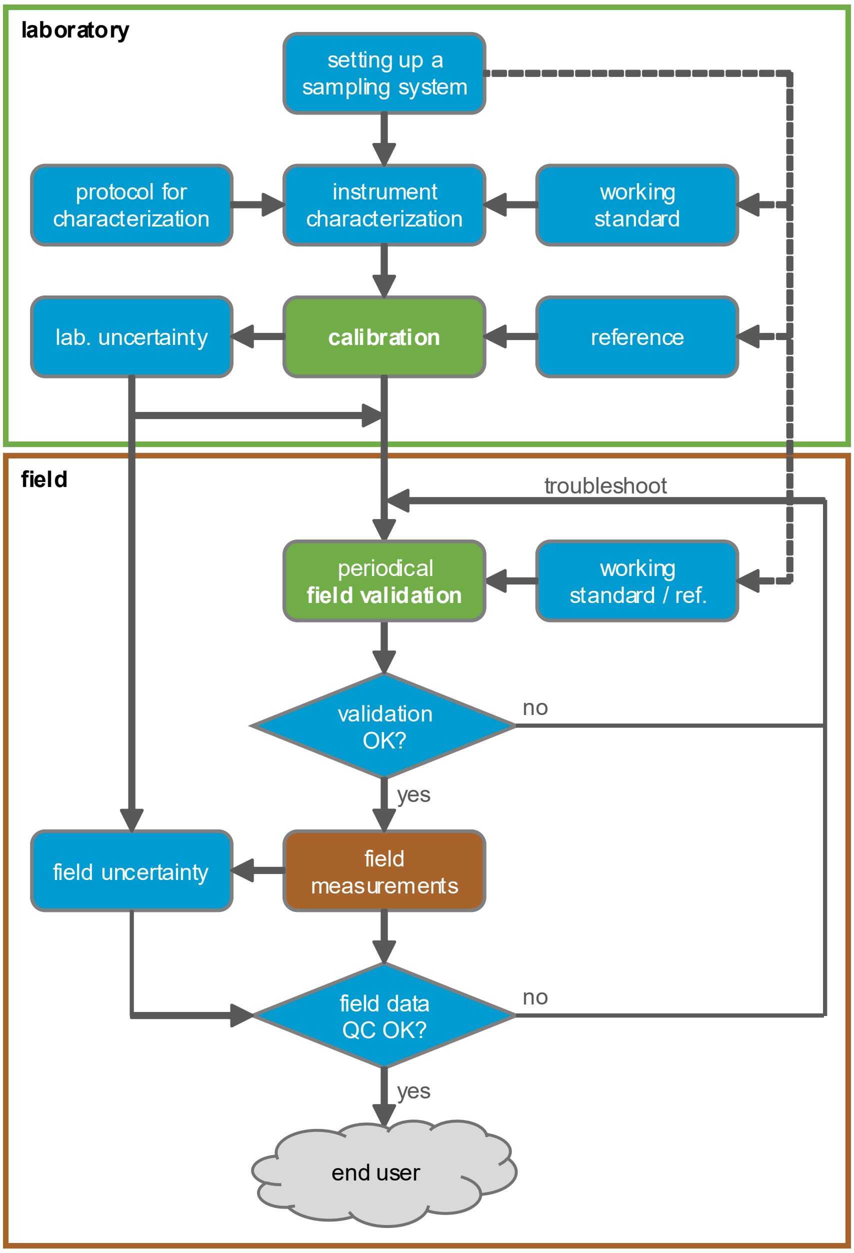

Figure 1: Flowchart showing the concept for metrological CH_4 field site measurements

The associated uncertainties to the field isotope results are calculated using the “laboratory” and the “field” uncertainties. The field uncertainty is estimated similarly to the laboratory uncertainty except that parameters like the instrument drift could have changed. Both uncertainty budgets (Laboratory and field) are estimated following the Guide to the Expression of Uncertainty (GUM) principles [5].

2.5 References

[1] C. Rennick et al.: Good practice guide for accurate methane isotope ratio measurements using laser spectroscopy: analyser characterisation and statement of uncertainty with a target precision of 0.2 ‰ for $\delta^{13}C$ (CH_4) and 1 ‰ for $\delta^{2}H$ $(CH)_4$, deliverable 6, EMPIR project 19ENV05 STELLAR, Oct. 2023, online: https://empir.npl.co.uk/stellarproject/documents/ (accessed: March 2024)

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