



Supplement of

Correction and calibration protocol for isotope data via CRDS: a study case for N₂O and other isotope systems

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1 Supplementary information

2 S.1 Experimental Setups and Workflows

3 Below, we provide a detailed description of the specific setup and conditions for each experiment conducted.

4 S.1.1 N₂O non-linearity (Exp. 1)

5 The experimental setup for Exp. 1 was designed to investigate the effect of N₂O concentrations on apparent δ -values. Nitrous
6 oxide target concentrations were set in the range of 0.350 to 1.200 ppm, depending on the CRDS investigated (See Section 3.1
7 for details). The target concentrations were achieved by adjusting calibration and dilution gas flows while maintaining a
8 constant total flow of 1000 mL min⁻¹ (Table S1). Each mixture was measured in triplicate across three independent experiments
9 to ensure reproducibility. A schematic of the gas mixing and measurement system is provided in Fig. S1.

10

11 **Table S1: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 1**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
N ₂ O (ppm)	0.35	0.425	0.5	0.575	0.65	0.725	0.8	0.99
<i>Target flows</i>								
Cal 1 / Cal 2	3.9	4.7	5.6	6.4	7.2	8.1	8.9	11.0
Dilution Gas	996.1	993.8	991.3	986.3	976.3	966.3	956.3	989.0
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments.

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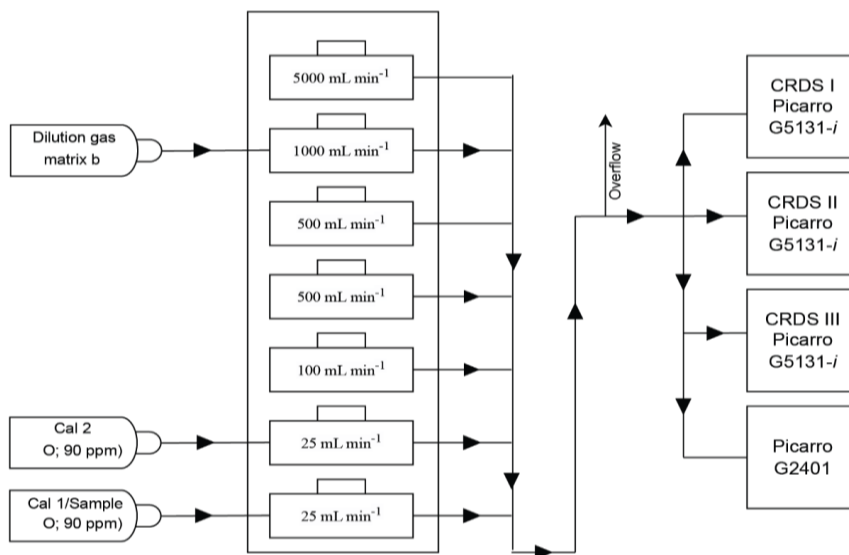


Figure S1: Schematic illustration of the experimental setup used for Exp. 1

S.1.2 CH₄ spectral interference (Exp. 2)

The experimental setup for Exp. 2 was designed to investigate the effect of CH₄ concentrations on apparent δ -values of N₂O. Nitrous oxide target concentrations were set to 0.330, 0.660, and 0.990 ppm, while CH₄ were changed in the range from 0.5 to 10 ppm, and was achieved by adjusting calibration and dilution gas flows while maintaining a constant total flow of 1000 mL min⁻¹ (Table S2–S4). Each mixture was measured in triplicate across three independent experiments to ensure reproducibility. A schematic of the gas mixing and measurement system is provided in Fig. S2.

Table S2: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 2

Parameter	Cal 1 / Cal 2	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
<i>Target concentrations</i>								
CH ₄ (ppm)	0	0.5	1	2	4	6	8	10
N ₂ O (ppm)	0.330	0.330	0.330	0.330	0.330	0.330	0.330	0.330
<i>Target flows</i>								
Cal 1 / Cal 2	3.67	3.67	3.67	3.67	3.67	3.67	3.67	3.67
Interferent test gas (CH ₄)	0	2.5	5	10	20	30	40	50
Dilution Gas	996.3	993.8	991.3	986.3	976.3	966.3	956.3	946.3
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments.

25 **Table S3: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 2**

Parameter	Cal 1 / Cal 2	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
<i>Target concentrations</i>								
CH ₄ (ppm)	0	0.5	1	2	4	6	8	10
N ₂ O (ppm)	0.330	0.666	0.666	0.666	0.666	0.666	0.666	0.666
<i>Target flows</i>								
Cal 1 / Cal 2	3.67	7.33	7.33	7.33	7.33	7.33	7.33	7.33
Interferent test gas (CH ₄)	0	2.5	5	10	20	30	40	50
Dilution Gas	992.7	990.2	987.7	982.7	972.7	962.7	952.7	942.7
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments.

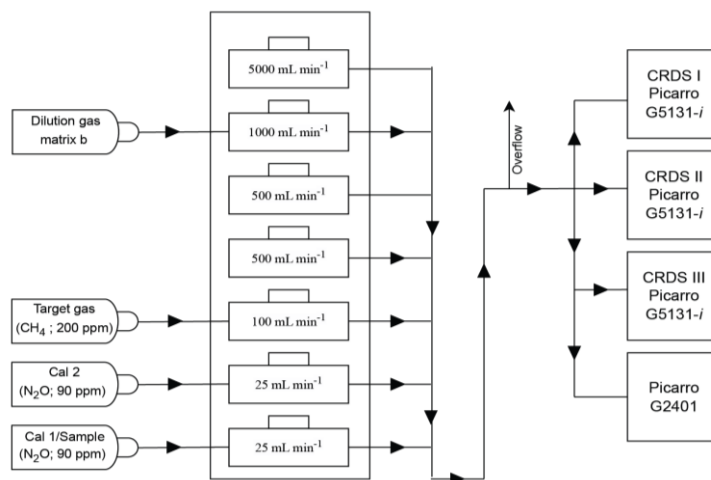
26

27 **Table S4: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 2**

Parameter	Cal 1 / Cal 2	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
<i>Target concentrations</i>								
CH ₄ (ppm)	0	0.5	1	2	4	6	8	10
N ₂ O (ppm)	0.330	0.990	0.990	0.990	0.990	0.990	0.990	0.990
<i>Target flows</i>								
Cal 1 / Cal 2	3.67	11	11	11	11	11	11	11
Interferent test gas (CH ₄)	0	2.5	5	10	20	30	40	50
Dilution Gas	992.7	986.5	984.0	979.0	969.0	959.0	949.0	939.0
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments.

28



29

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Figure S2: Schematic illustration of the experimental setup used for Exp. 2

31 **S.1.3 CO₂ spectral interference (Exp. 3)**

32 The experimental setup for Exp. 3 was designed to investigate the effect of CO₂ concentrations on apparent δ -values of N₂O.
 33 Nitrous oxide target concentrations were set to 0.330, 0.660, and 0.990 ppm, while CO₂ were changed in the range from 0 to
 34 2000 ppm, and was achieved by adjusting calibration and dilution gas flows while maintaining a constant total flow of 1000
 35 mL min⁻¹ (Table S5–S7). Each mixture was measured in triplicate across three independent experiments to ensure
 36 reproducibility. A schematic of the gas mixing and measurement system is provided in Fig. S3.

37
 38 **Table S5: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 3**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
CO ₂ (ppm)	0	0	250	500	750	1000	1500	2000
N ₂ O (ppm)	0.330	0.330	0.330	0.330	0.330	0.330	0.330	0.330
<i>Target flows</i>								
Cal 1 / Cal 2	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7
Interferent test gas (CO ₂)	0.0	0.0	6.3	12.5	18.8	25.0	37.5	50.0
Dilution Gas	996.3	996.3	990.1	983.8	977.6	971.3	958.8	946.3
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments.

39

40 **Table S6: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 3**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
CO ₂ (ppm)	0	0	250	500	750	1000	1500	2000
N ₂ O (ppm)	0.330	0.660	0.660	0.660	0.660	0.660	0.660	0.660
<i>Target flows</i>								
Cal 1 / Cal 2	3.7	7.3	7.3	7.3	7.3	7.3	7.3	7.3
Interferent test gas (CO ₂)	0.0	0.0	6.3	12.5	18.8	25.0	37.5	50.0
Dilution Gas	996.3	992.7	986.4	980.2	973.9	967.7	955.2	942.7
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments.

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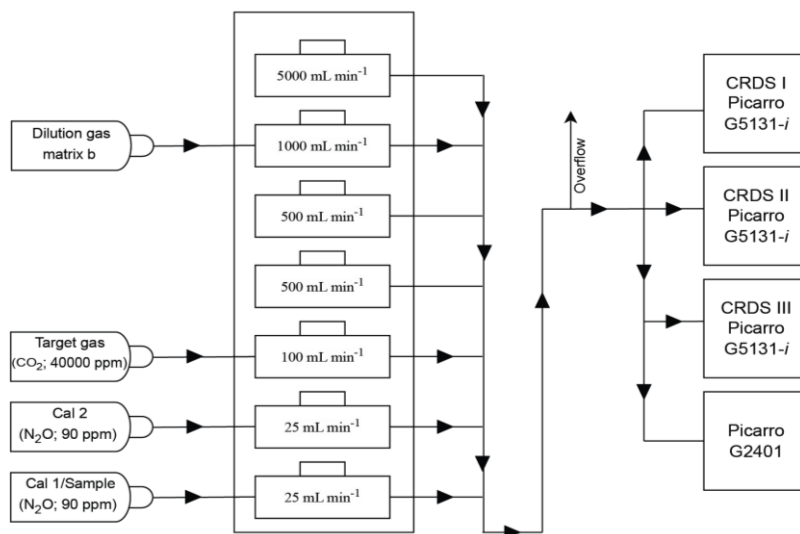
43

44

45 **Table S7: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 3**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
CO ₂ (ppm)	0	0	250	500	750	1000	1500	2000
N ₂ O (ppm)	0.330	0.990	0.990	0.990	0.990	0.990	0.990	0.990
<i>Target flows</i>								
Cal 1 / Cal 2	3.7	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Interferent test gas (CO ₂)	0.0	0.0	6.3	12.5	18.8	25.0	37.5	50.0
Dilution Gas	996.3	989.0	982.8	976.5	970.3	964.0	951.5	939.0
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

46 *Each sample configuration was measured three times in three independent experiments.*



48 **Figure S3: Schematic illustration of the experimental setup used for Exp. 3**

49 **S.1.4 O₂ matrix gas effect (Exp. 4)**

50 The experimental setup for Exp. 4 was designed to investigate the effect of O₂ concentrations on apparent δ -values of N₂O.
 51 Nitrous oxide target concentrations were set to 0.330, 0.660, and 0.990 ppm, while O₂ were diluted down from ~21 to ~0%,
 52 achieved by adjusting calibration and dilution gas flows while maintaining a constant total flow of 1000 mL min⁻¹ (Table S8–
 53 S10). Each mixture was measured in triplicate across three independent experiments to ensure reproducibility. A schematic of
 54 the gas mixing and measurement system is provided in Fig. S4. Please note that the target oxygen concentrations were set at
 55 12, 14, 16, 20, and 20.7%. However, since the *Cal 1* and *Cal 2* reference gases contribute an additional matrix baseline of
 56 approximately 770, 1544, and 2316 ppm O₂ at N₂O concentrations of 330, 660, and 990 ppb, respectively, meaning that target
 57 O₂ values do not start from zero as they do for N₂O.
 58

59 **Table S8: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 4**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
O ₂ (ppm)	770	770	120000	140000	160000	180000	200000	207000
N ₂ O (ppm)	0.330	0.330	0.330	0.330	0.330	0.330	0.330	0.330
<i>Target flows</i>								
Cal 1 / Cal 2	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7
Interferent test gas (O ₂)	0.0	0.0	572.8	668.3	763.7	859.2	954.7	988.1
Dilution Gas (N ₂)	996.3	996.3	423.5	328.1	232.6	137.1	41.7	8.3
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments, and all flows are in mL/min

60

61 **Table S9: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 4**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
O ₂ (ppm)	770	1544	120000	140000	160000	180000	200000	207000
N ₂ O (ppm)	0.330	0.660	0.660	0.660	0.660	0.660	0.660	0.660
<i>Target flows</i>								
Cal 1 / Cal 2	3.7	7.3	7.3	7.3	7.3	7.3	7.3	7.3
Interferent test gas (O ₂)	0.0	0.0	572.8	668.3	763.7	859.2	954.7	988.1
Dilution Gas (N ₂)	996.3	992.7	419.9	324.4	228.9	133.5	38.0	4.6
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments, and all flows are in mL/min

62

63 **Table S10: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 4**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 6</i>	<i>Sample 7</i>
<i>Target concentrations</i>								
O ₂ (ppm)	770	2316	120000	140000	160000	180000	200000	207000
N ₂ O (ppm)	0.330	0.990	0.990	0.990	0.990	0.990	0.990	0.990
<i>Target flows</i>								
Cal 1 / Cal 2	3.7	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Interferent test gas (O ₂)	0.0	0.0	572.8	668.3	763.7	859.2	954.7	988.1
Dilution Gas (N ₂)	996.3	989.0	416.2	320.7	225.3	129.8	34.3	0.9
Total flow	1000	1000	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments, and all flows are in mL/min

64

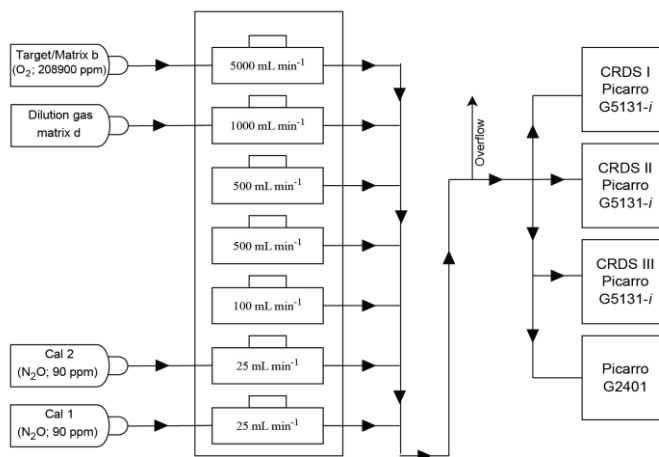


Figure S4: Schematic illustration of the experimental setup used for Exp. 4

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68

69 S.1.5 Validation experiments to test combined effects of N₂O, CH₄ and CO₂ concentration changes (Exp. 5)

70 The experimental setup for Exp. 5 was designed to investigate the combined effects of CO₂ and CH₄ on apparent δ -values of
 71 N₂O. Nitrous oxide target concentrations were set to 0.330 and 0.660. Carbon dioxide and methane were simultaneously varied
 72 from 0 to 2000 ppm and 0 to 10 ppm, respectively, over five steps (Table S11–S12). Each mixture was measured in triplicate
 73 across three independent experiments to ensure reproducibility. A schematic of the gas mixing and measurement system is
 74 provided in Fig. S5.

75

76 **Table S11: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–5) Exp. 5a**

<i>Parameter</i>	<i>Cal 1 / Cal 2</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 4</i>	<i>Sample 5</i>
<i>Target concentrations</i>						
CH ₄ (ppm)	0	0	2.5	5	7.5	10
CO ₂ (ppm)	0	0	500	1000	1500	2000
N ₂ O (ppm)	0.330	0.330	0.330	0.330	0.330	0.330
<i>Target flows</i>						
Cal 1 / Cal 2	3.7	3.7	3.7	3.7	3.7	3.7
Interferent test gas (CH ₄)	0.0	0.0	12.8	25.6	38.4	51.2
Interferent test gas (CO ₂)	0.0	0.0	12.7	25.4	38.0	50.7
Dilution Gas	996.3	996.3	970.9	945.4	919.9	894.4

Total flow 1000 1000 1000 1000 1000 1000

Each sample configuration was measured three times in three independent experiments, and all flows are in mL/min

77

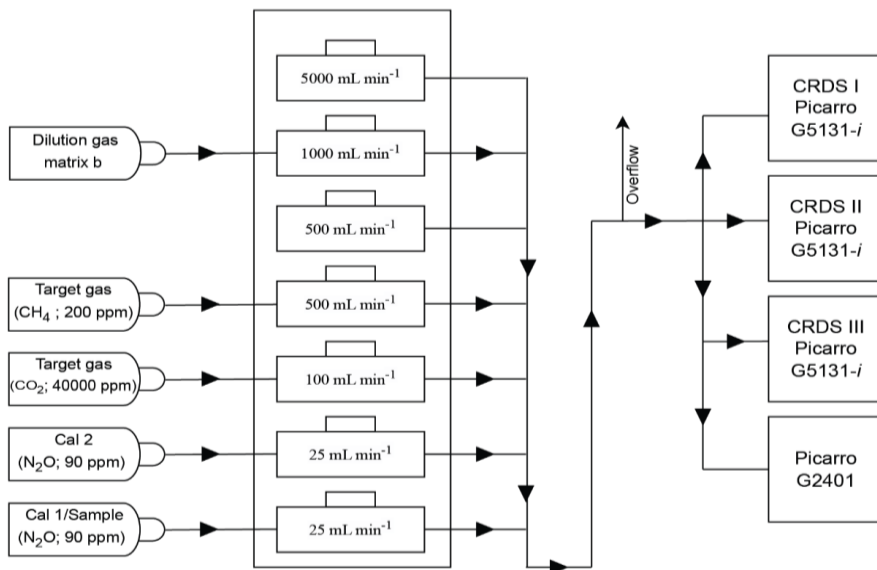
78 **Table S12: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–5) in Exp. 5b**

Parameter	Cal 1 / Cal 2	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
<i>Target concentrations</i>						
CH ₄ (ppm)	0	0	2.5	5	7.5	10
CO ₂ (ppm)	0	0	500	1000	1500	2000
N ₂ O (ppm)	0.660	0.660	0.660	0.660	0.660	0.660
<i>Target flows</i>						
Cal 1 / Cal 2	7.3	7.3	7.3	7.3	7.3	7.3
Interferent test gas (CH ₄)	0.0	0.0	12.8	25.6	38.4	51.2
Interferent test gas (CO ₂)	0.0	0.0	12.7	25.4	38.0	50.7
Dilution Gas	992.6	992.6	967.2	941.7	916.2	890.8
Total flow	1000	1000	1000	1000	1000	1000

Each sample configuration was measured three times in three independent experiments

All flows are in mL/min

79



80 **Figure S5: Schematic illustration of the experimental setup used for Exp. 5**

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83 **S.1.6 Validation of dynamic versus static dilution of reference gases (Exp. 6)**

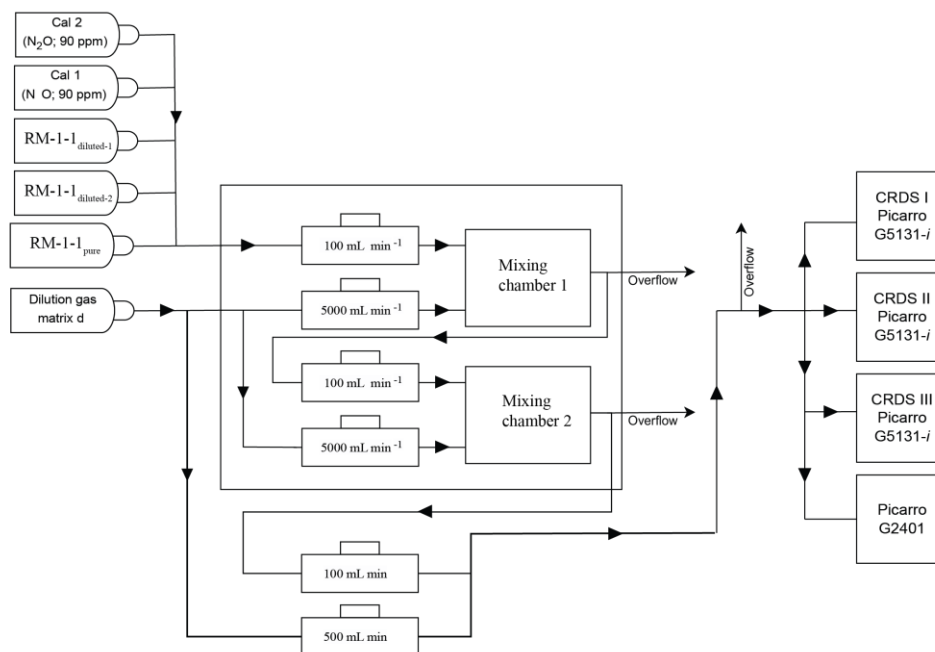
84 The experimental setup for Exp. 6 was designed to test the difference between dynamic and static dilution of the same reference
 85 gas. Nitrous oxide was diluted down to ambient concentrations from a pure N₂O standard (RM-1-1_{pure}). This was achieved
 86 using a custom-built two-step diluter provided by the Swiss National Metrology Institute (METAS), followed by a third
 87 dilution step with standalone MFC boxes. A schematic of the gas mixing and measurement system is provided in Fig. S6,
 88 while Table S13 provides an overview of the dilution process.

89

90 **Table S13: Target concentrations and flow settings for calibration and sample mixtures (Samples 1–7) in Exp. 6**

Dilution device	Step	RM-1-1 _{pure} (N ₂ O ppm)	Target (N ₂ O ppm)	Total flow	MFC #1, (RM-1-1 _{pure})	MFC #2 (Matrix b)
two-step diluter (Metas)	1.1 (Ch. #1)	1000000	3000	5005	15	4985
	1.2 (Ch. #2)	3000	10	5000	17	4983
MFC (Vögtlin Instruments)	2 (Extra dil.)	10	0.330	500	16.5	483.5

All flows are in mL/min. RM-1-1_{Diluted-1} and RM-1-1_{Diluted-2} have ambient N₂O concentrations and therefore were introduced without dilution. For Cal 1 and 2, both at ~90 ppm, were diluted in a single step using Mixing Chamber 1, identical to the general experimental setup (See for example, Table 2).



92

93 **Figure S6: Schematic illustration of the experimental setup used for Exp. 6. RM-1-1_{Diluted-1} and RM-1-1_{Diluted-2} have ambient N₂O**
 94 **concentrations and were therefore routed directly through the system without the use of a dilution gas. Cal 1 and Cal 2 were diluted**
 95 **in a single step in mixing chamber 1, analogous to the general experimental setup, with flow rates as given for example in Table S2.**
 96 **RM-1-1_{Pure} was diluted dynamically to ambient concentrations via the three-step dilution scheme described in Table S13.**

97 **S2 Results: dynamic versus static dilution comparison (Exp. 6)**

98 We conducted a study to validate the preparation of statically diluted standards (RM-1-1_{Diluted-1} and
 99 RM-1-1_{Diluted-2}; Table 1), which might be subject to fractionation effects during preparation, against dynamically
 100 prepared gases

101 starting from the same pure N₂O reference gas (RM-1-1_{Pure}; Table 1). The key distinction is that RM-1-1_{pure} is
 102 an

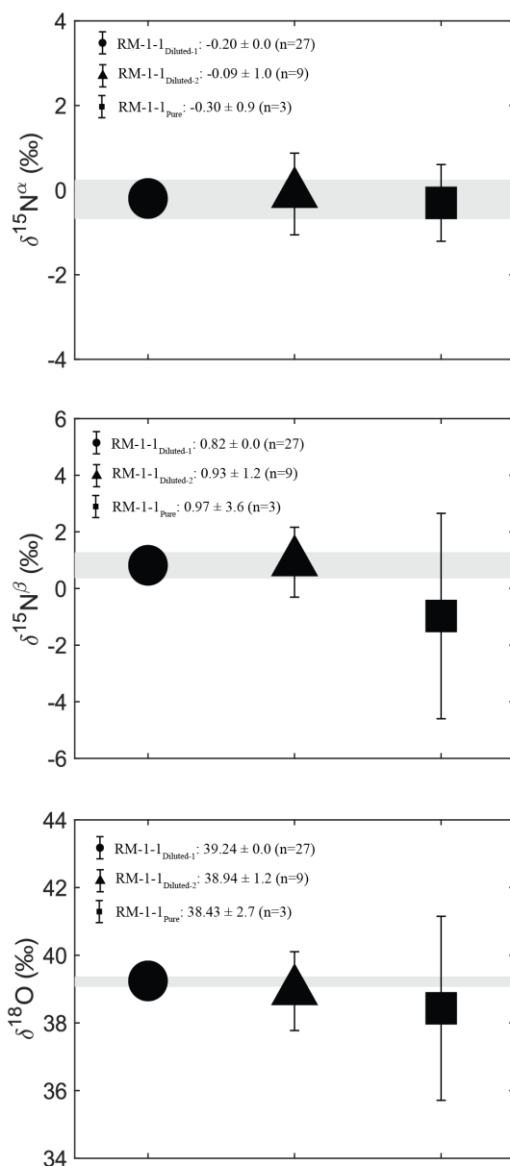
103 undiluted pure N₂O standard, while RM-1-1_{Diluted-1} and RM-1-1_{Diluted-2} are gravimetrically prepared
 104 ambient-concentration dilutions of the same gas (~327; Table 1), which were prepared according to Mohn et al.
 105 (2014). The dynamic dilution approach prepares the same gas at ambient concentration in real time using a
 106 sequence of dilution

107 steps. To facilitate dynamic dilution from pure gases to ambient concentrations (330 ppb N₂O), i.e. by a factor of
 108 3.3×10^6 , a custom-built two-step diluter provided by the Swiss Federal Institute of Metrology (METAS),
 109 was

applied. Given the very low flows of pure N₂O provided, an extensive stabilisation period of 1 hour was applied,
 with data from the last 5 minutes used for further analysis. The statically diluted standard gases were measured
 for

110 of RM-1-1_{Diluted-1} and Cal 2.1_{330ppb} were bracketing the measuring phase (phase 2). During the measuring phase,
111 each sample gas measurement was bracketed by measurement of the RM-1-1_{Diluted-1} standard gas to continuously
112 assess the analyser's stability and post-correct for any analytical drift.

113 Results from comparing dynamic versus static dilutions of the same initial pure N₂O gas (RM-1-1_{pure}) show no
114 significant differences between the two approaches (Fig. S7). For $\delta^{15}\text{N}^{\alpha}$, both the statically diluted N₂O gas (RM-
115 1-1_{Diluted-2}) and the dynamically diluted N₂O gas (diluted from RM-1-1_{pure}) fall within the assigned value of $-0.22 \pm$
116 0.46 ‰ (SD) , with RM-1-1_{Diluted-2} registering at $-0.09 \pm 1 \text{ ‰ (SD)}$ and RM-1-1_{pure} $-0.30 \pm 0.9 \text{ ‰ (SD)}$. Concerning
117 $\delta^{15}\text{N}^{\beta}$, the statically diluted N₂O gas agrees better with the original pure N₂O, with a value of $0.93 \pm 1.2 \text{ ‰ (SD)}$
118 relative to the assigned value of $0.82 \pm 0.46 \text{ ‰ (SD)}$, while the dynamically diluted N₂O gas displays large
119 variability within $-0.97 \pm 3.6 \text{ ‰ (SD)}$. Lastly, a similar trend is seen for $\delta^{18}\text{O}$, where the static dilution approach
120 exhibits a value of $38.94 \pm 1.2 \text{ ‰ (SD)}$, in line with the assigned value of $39.22 \pm 0.15 \text{ ‰ (SD)}$, while the dynamic
121 dilution displays a slightly lower number of $38.43 \pm 2.7 \text{ ‰ (SD)}$. For the dynamically diluted calculations, only
122 data points where the post-processed data had a standard deviation below 8 ‰ were included in the analyses. In
123 summary, no significant offsets in isotopic composition between statically and dynamically prepared ambient
124 concentration N₂O reference gases were detected, which indicates the absence of substantial fractionation effects.
125 Dynamically prepared N₂O reference gases, however, display large variability in N₂O isotopic composition, in
126 particular for $\delta^{15}\text{N}^{\beta}$. This effect might not be a fractionation effect, which is supposed to impart all isotopic
127 dimensions, but an apparent effect due to variability in the gas composition (e.g. N₂O concentration), provided the
128 very high dilution ratios. Results also indicate that the applied two-step dynamic dilution is not a suitable approach
129 to provide N₂O reference gases at 330 ppb N₂O at sufficient stability to perform instrument calibration.



131 **Figure S7:** Isotopic composition, $\delta^{15}\text{N}^\alpha$, $\delta^{15}\text{N}^\beta$, $\delta^{18}\text{O}$ in N_2O reference gases prepared by static dilution (RM-1-1_{Diluted-2}) and
 132 dynamic dilution from a pure N_2O gas (RM-1-1_{pure}) (see Table 1) measured on CRDS II. The grey box represents the isotopic
 133 composition \pm its uncertainty ($\delta^{15}\text{N}^\alpha = -0.22 \pm 0.46$ ‰, $\delta^{15}\text{N}^\beta = 0.82 \pm 0.46$ ‰, $\delta^{18}\text{O} = 39.22 \pm 0.15$ ‰) of a statically diluted
 134 N_2O reference gas used for comparison (RM-1-1_{Diluted-1}).

135 S3 Uncertainty Evaluation and Error Propagation

136 S.3.1 Input parameters

137 Calibration-based measurement models, commonly used for CRDS analysers and similar devices, present the
138 challenge that each applied correction introduces its own inherent uncertainty. To better understand and pinpoint
139 the primary sources of error and gain deeper insight into their influence on the overall measurement uncertainty,
140 we conducted an uncertainty evaluation using the error propagation of up to 7 parameters per delta value. These
141 parameters include the regression slopes (m_{N_2O} , m_{CH_4} , m_{CO_2}) used for the trace gas-related corrections (N_2O , CH_4
142 and CO_2), the δ -values of the applied isotopic reference gases, and an additional term due to poorly-understood
143 effects, related to instrumental drifts and other uncharacterised aspects of the measurement system. This could be
144 expressed by the standard deviation of repeated target gas analyses. The uncertainties were evaluated using the
145 GUM guideline (BIPM et al., 2008; JCGM, 2008) and using the law of propagation of uncertainty to yield the
146 combined standard uncertainty

147

$$148 \quad \sigma^2 (f(x_i)) = \sum_{i=1}^N \left(\sigma^2(x_i) * \left(\frac{\partial f}{\partial x_i} \right)^2 \right) * u^2(x_i)$$

149

150 *Where* f is the mathematical model reported in Appendix A, x_i is the input quantity, and $u(x_i)$ the uncertainty of
151 each of the input variables. The partial derivatives are provided in Appendix A and describe how
152 sensitive the measurand responds to changes in a given input variable. In the implemented error analysis, we
153 anticipate that the applied mathematical measurement model is correct, i.e. correction terms are additive and
154 constant in time. As spectral interferences were observed to be non-additive and the N_2O non-linearity was
155 found to be variable in time (see Section 3), the uncertainty evaluation implemented in the MATLAB code is
156 only valid for a best case and should be taken with care.

157 S.3.2 Example of uncertainty budget

158 To provide an exemplary uncertainty estimate, we evaluated the uncertainty components for experiment 2 (sec. 3.2) performed
159 at 330 ppb N_2O (Cal-1) with different additions in CH_4 (up to 10 ppm). In detail, measurements on 05.02.2024 with CRDS-I
160 were evaluated. The following input parameters for the uncertainty calculations were considered; the uncertainties in the N_2O
161 non-linearity correction slope (Δm_{N_2O}), the CH_4 correction slope (Δm_{CH_4}), and the isotopic composition of $Cal_{1,1}$ and $Cal_{2,1}$
162 reference gases, provided in Tables 4, 5, and 1, respectively. The uncertainty contribution by the N_2O concentration correction
163 (Eq. A20) is negligible for all delta values (< 0.01 %), since sample and reference gases are measured at similar N_2O

164 concentration (330 ppb). The uncertainty due to "imperfect" CH₄ spectral interference correction (Eq. A21) increases with
165 increasing CH₄ concentration, up to 0.23 ‰ in $\delta^{15}\text{N}^{\alpha}$, 0.13 ‰ in $\delta^{15}\text{N}^{\beta}$ and 0.05 ‰ in $\delta^{18}\text{O}$ for the highest CH₄ sample (10
166 ppm). The propagated uncertainty due to the calibration correction (Eq. A23-A24) is approximately 0.31 ‰ in $\delta^{15}\text{N}^{\alpha}$, 0.11 ‰
167 in $\delta^{15}\text{N}^{\beta}$, and 0.35 ‰ in $\delta^{18}\text{O}$. The uncertainty due to poorly understood effects, estimated by the repeatability of target gas
168 measurements, is 0.5 ‰ for all isotopologues. The total uncertainties (Eq. A19) for the N₂O sample gas with 10 ppm CH₄
169 sample are 0.63 ‰, 0.53 ‰, 0.62 ‰ for $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$, respectively.

170 **References**

- 171 BIPM, I., Ifcc, I., & Iso, I. (2008). IUPaP, and OImL. *Evaluation of measurement data—Supplement, 1*.
- 172 JCGM, J. (2008). Evaluation of measurement data—Guide to the expression of uncertainty in measurement. *Int. Organ.*
173 *Stand. Geneva ISBN, 50*, 134.
- 174 Mohn, J., Wolf, B., Toyoda, S., Lin, C. T., Liang, M. C., Brüggemann, N., Wissel, H., Steiker, A. E., Dyckmans, J., &
175 Szwec, L. (2014). Interlaboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass
176 spectrometry and laser spectroscopy: current status and perspectives. *Rapid Communications in Mass Spectrometry*,
177 *28*(18), 1995–2007.
- 178