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Concentration dependence and scale linearity of the carbon isotope ratio measurement systems based on CRDS

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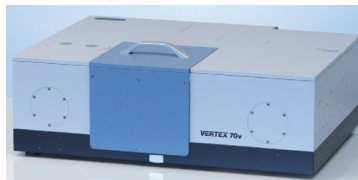
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Outline

▷ **Introduction**

▷ **Experimental**

▷ **Results and discussion**

▷ **Conclusion**

Introduction

ISOTOPE RATIO INFRARED SPECTROMETERS

Advantages

▷ Experimental usability, field deployability and low cost of the optical instruments

▷ $^{16}O\,^{13}C\,^{16}O$ vs $^{16}O\,^{12}C\,^{17}O$
$m_1=m_2$ ⇒ impossible for traditional IRMS
$\nu_1 \neq \nu_2$ ⇒ easy for IRIS

▷ Quantum chemistry ⇒ Line intensities ⇒ Calibration free measurements (U<0.5 % nowadays)

Disadvantages

▷ Low accuracy
Testing routine and corrections are not developed
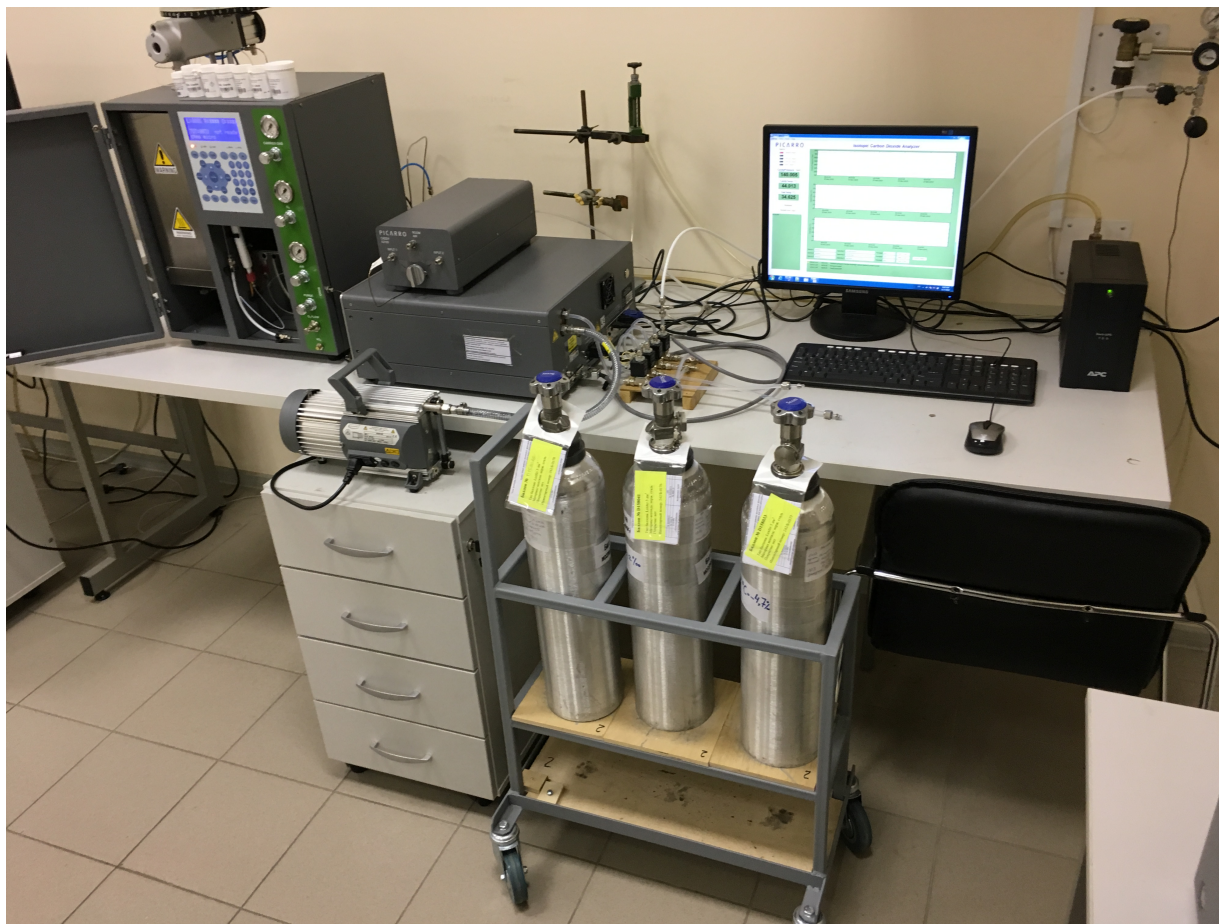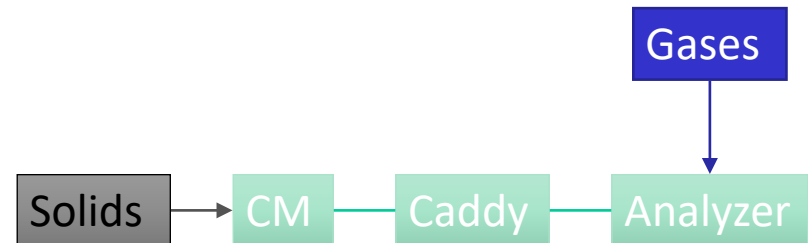
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Experimental

CM-CRDS carbon isotope ratio measurement facility

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Experimental

CM-CRDS carbon isotope ratio measurement facility:

▷ Picarro G2131i analyzer

▷ Picarro combustion module

▷ Picarro Caddy Universal interface

Gases → Analyzer

Solids → CM — Caddy — Analyzer

Validation of the facility:

▷ CCQM-P175: Carbon Stable Isotope Ratio Delta Values in Honey (2017)

▷ CCQM-K167/P211: Carbon isotope delta measurements of vanillin (on-going)

▷ CCQM-P212: Coherence of carbon isotope delta reference materials (on-going)

▷ CCQM-P204: CO2 Isotope Ratios ($\delta13C$ and $\delta18O$) in pure CO2 (on-going)

CRM's for calibration: IAEA-NBS-22, IAEA-CH-7, IAEA-CH-3, IAEA-600, UME CRM 1312
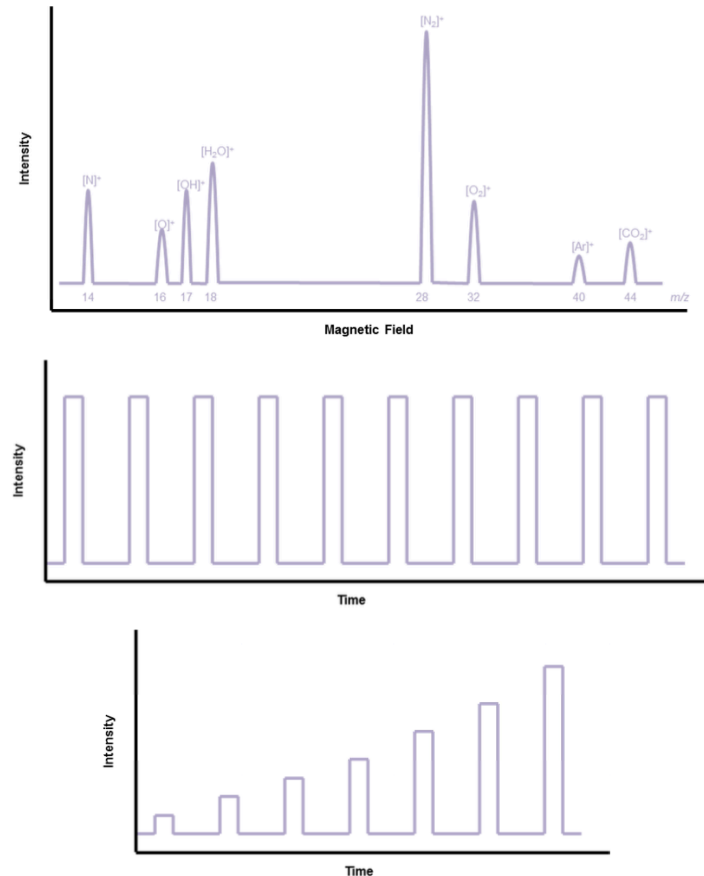
Results and discussion

IRMS basic testing routine*

▷ Background gases+blank test

▷ Stability (on-off test)
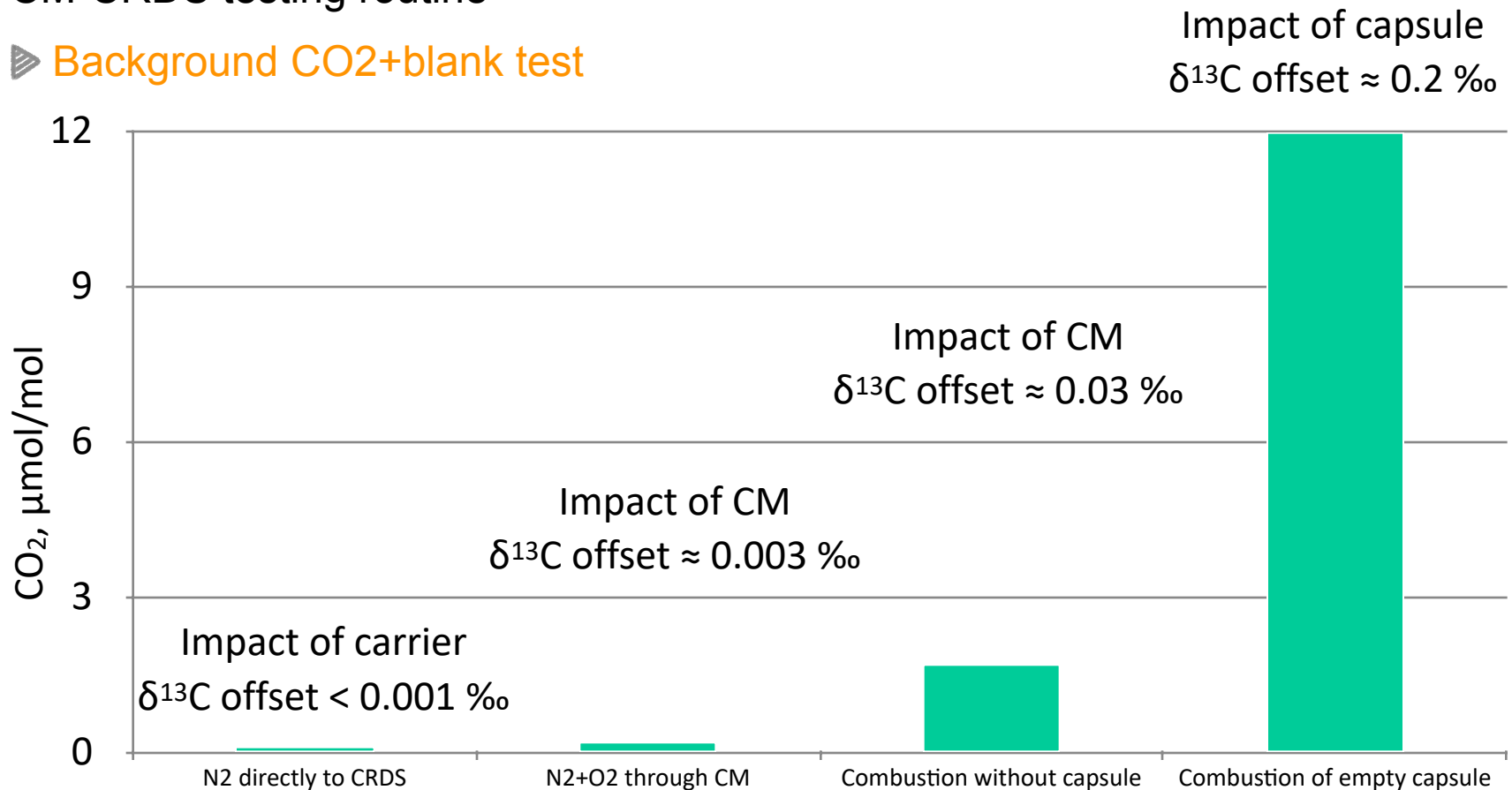
▷ Linearity (peak size)

* All tests and corrections can be found at Dunn P. J. H. and J. F. Carter, eds. 2018. Good practice guide for isotope ratio mass spectrometry, 2nd edition. FIRMS. ISBN 978-0-948926-33-4

Results and discussion
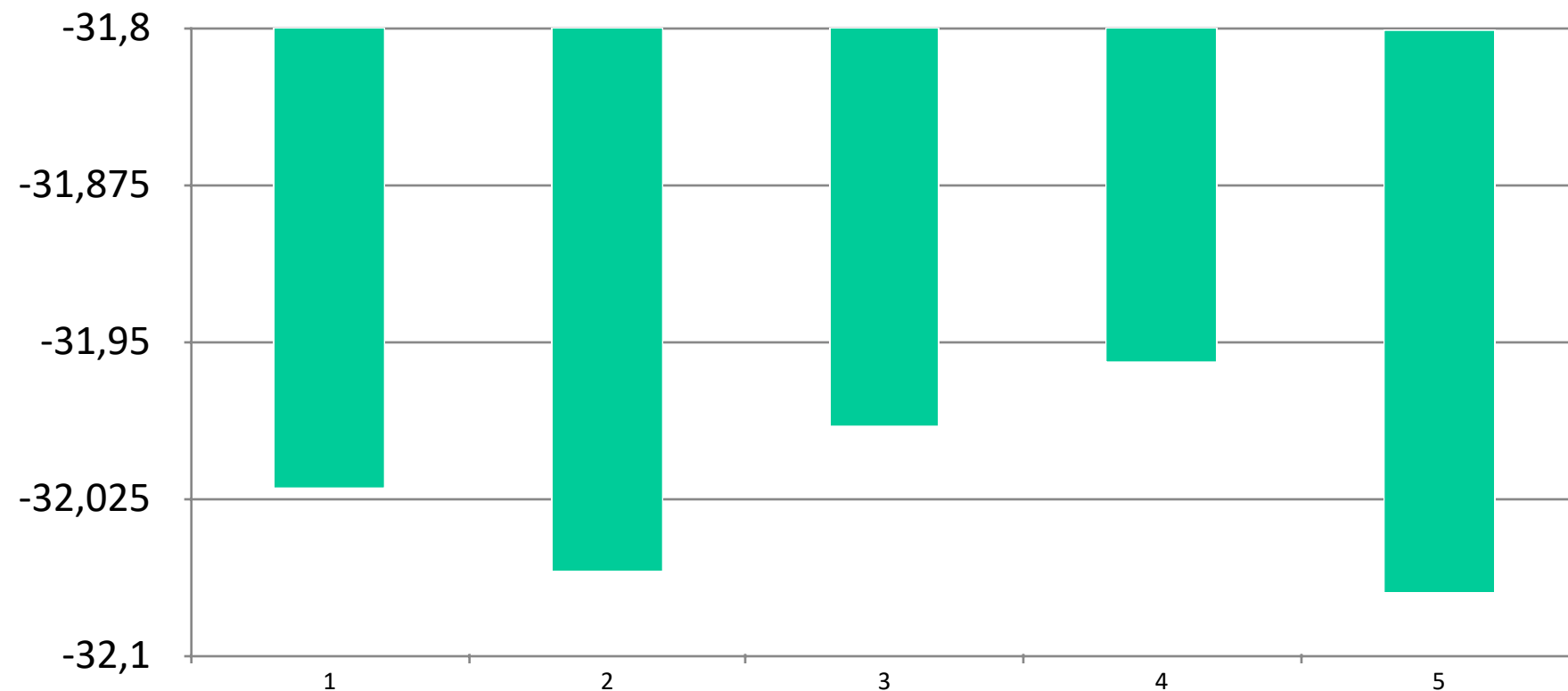
CM-CRDS testing routine

▷ Background CO2+blank test

Impact of capsule
$\delta^{13}C$ offset ≈ 0.2 ‰

Impact of CM
$\delta^{13}C$ offset ≈ 0.03 ‰

Impact of CM
$\delta^{13}C$ offset ≈ 0.003 ‰

Impact of carrier
$\delta^{13}C$ offset < 0.001 ‰

Y-axis: CO_2, μmol/mol (0, 3, 6, 9, 12)

X-axis categories: N2 directly to CRDS | N2+O2 through CM | Combustion without capsule | Combustion of empty capsule

Results and discussion

CM-CRDS testing routine

▷ Stability (on-off test)

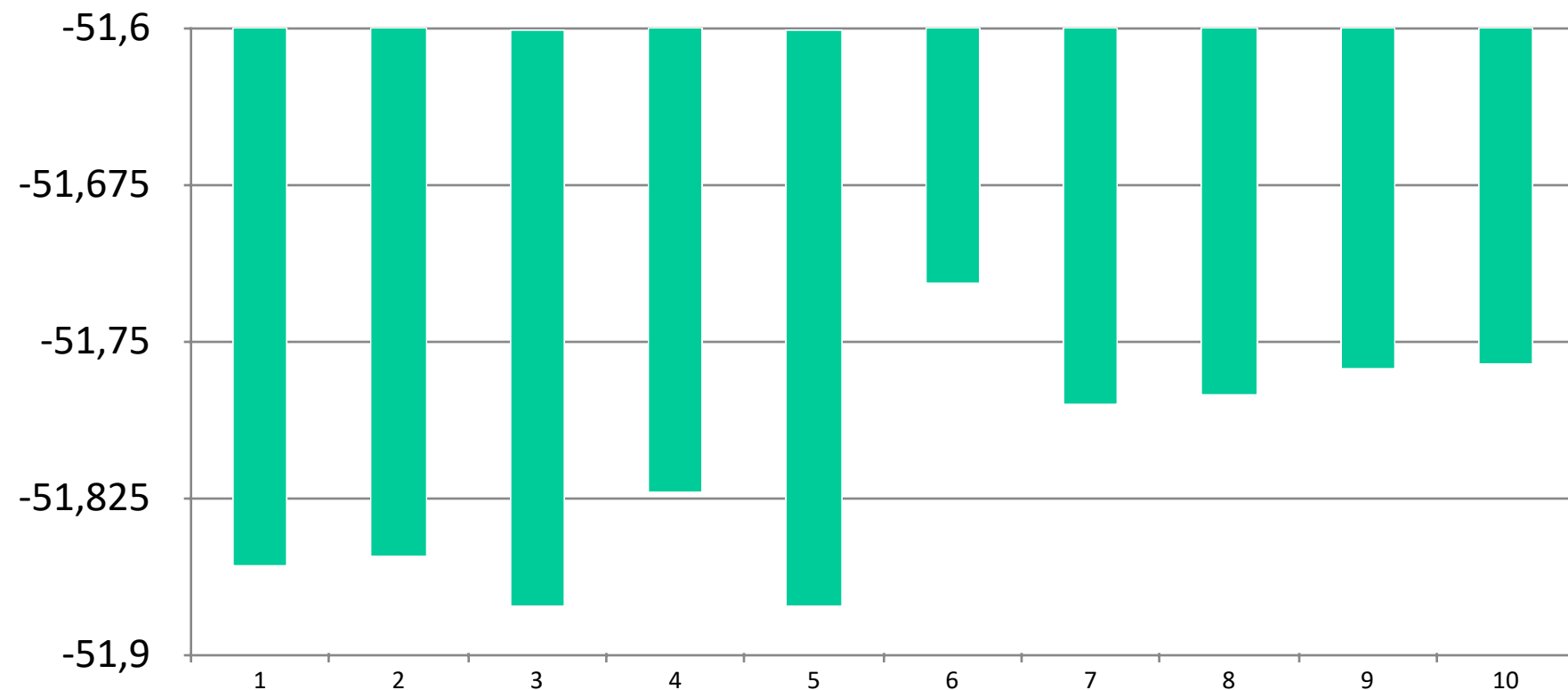Solid sample (acetanilide)
SD(δ^{13}C)=0.05 ‰

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Results and discussion

CM-CRDS testing routine

▷ Stability (on-off test)
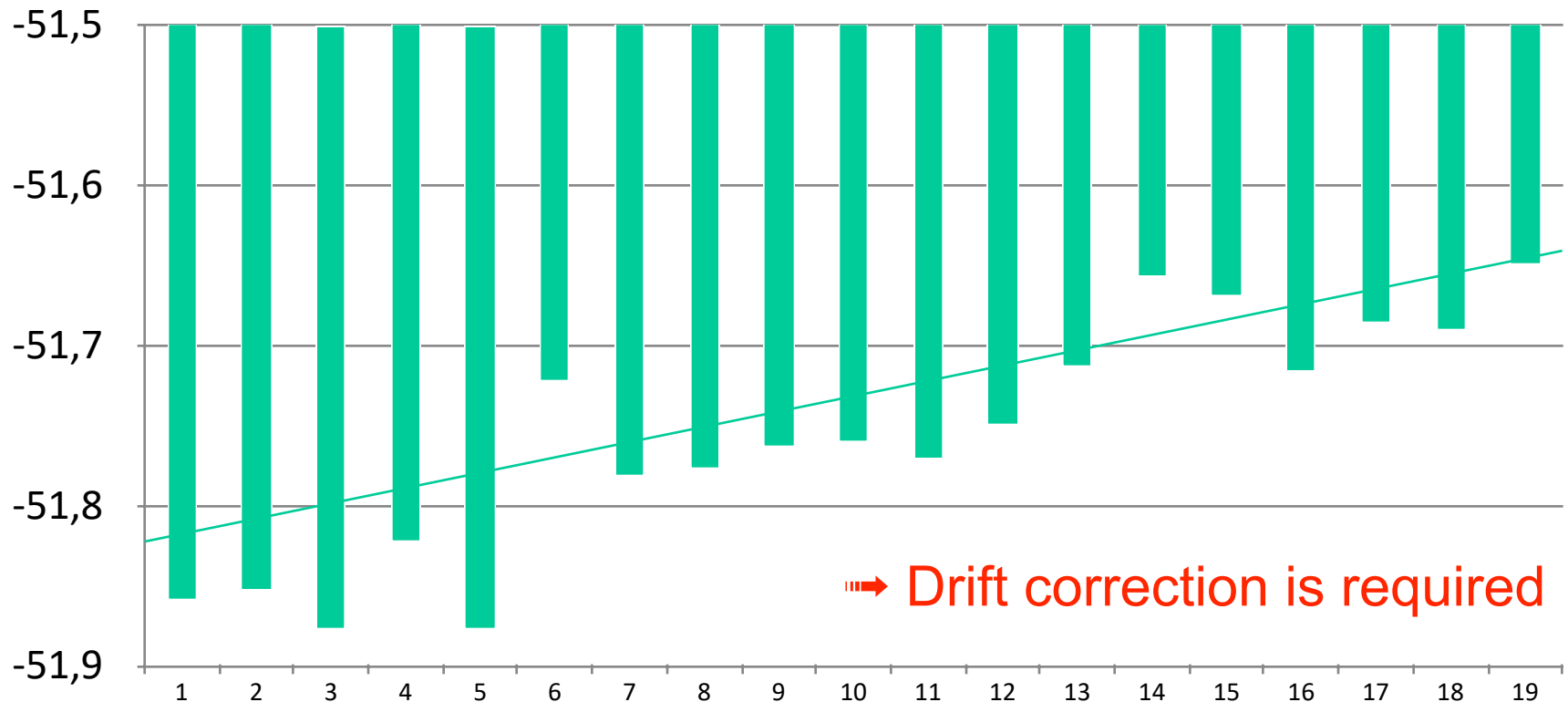
Gas sample (CO2+N2)
$SD(\delta^{13}C)=0.05$ ‰

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Results and discussion

CM-CRDS testing routine

Gas sample ($CO_2 + N_2$)

drift ($\delta^{13}C$) ≈ 0.2 ‰
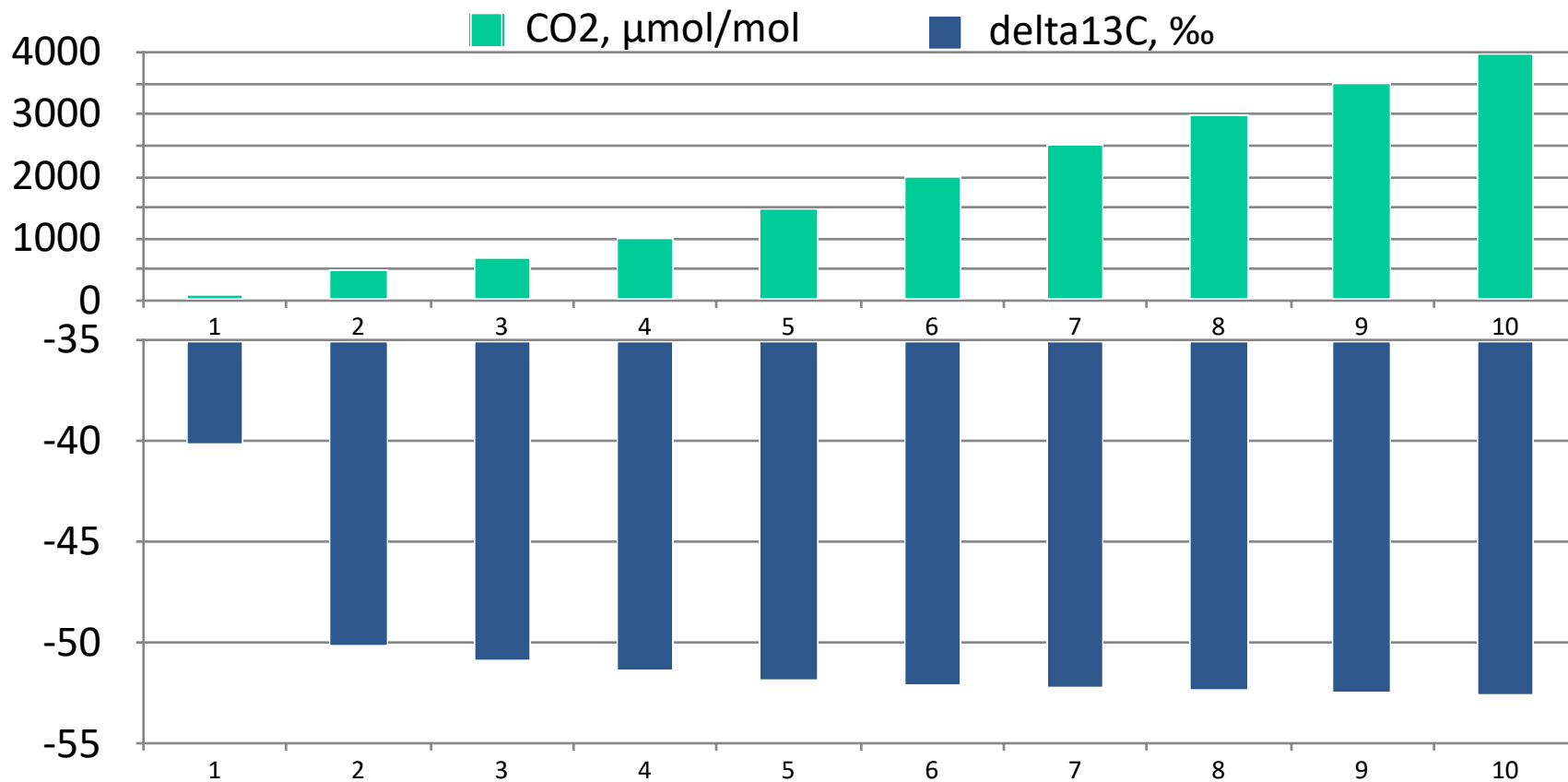
t = 340 min

▷ Stability (on-off test)

➡ Drift correction is required

Results and discussion

CM-CRDS testing routine

▷ Linearity (peak size)

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Results and discussion

CM-CRDS testing routine

▷ Linearity (peak size)

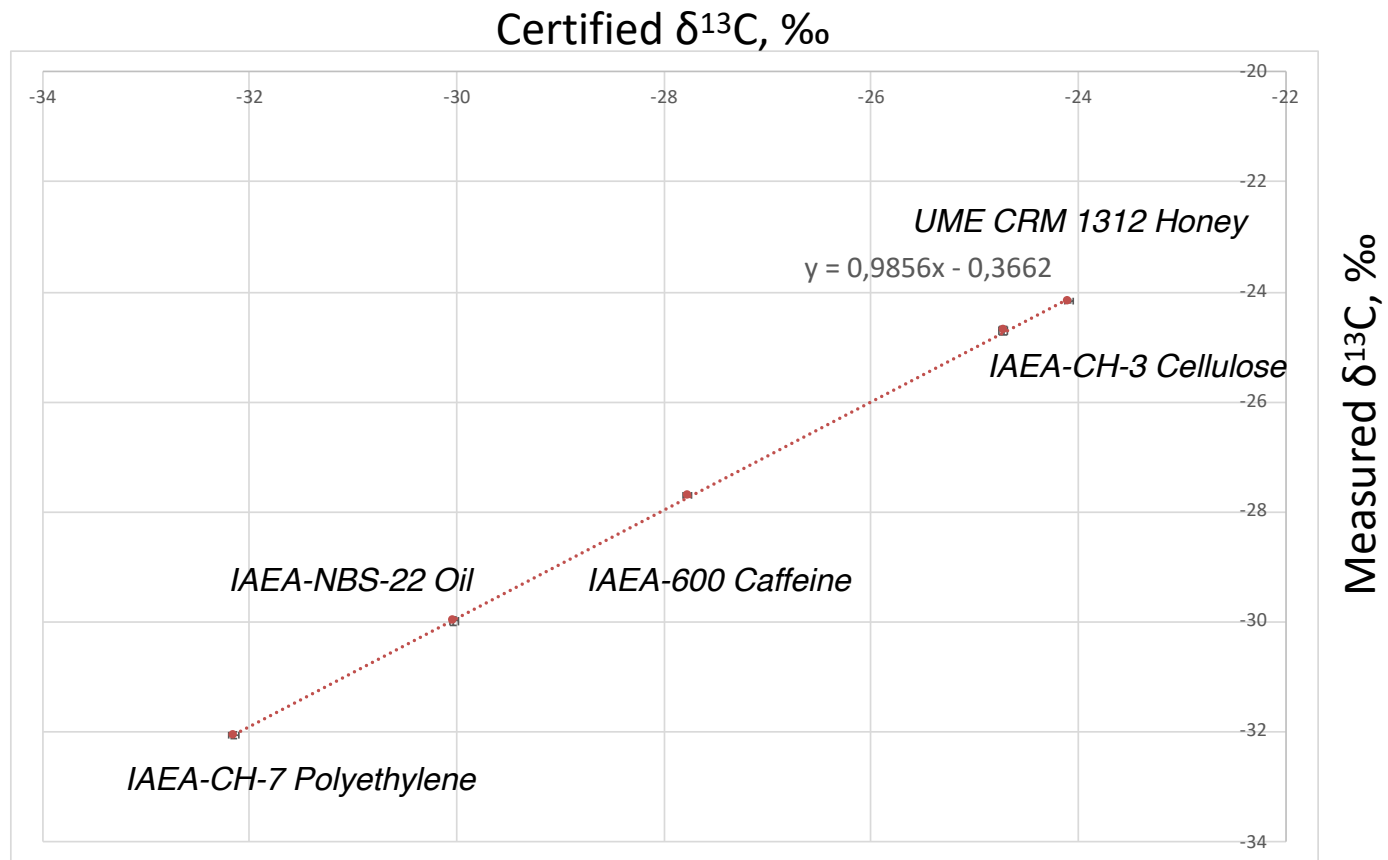| Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	0,01025		
Adj. R-Square	0,99909		
		Value	Standard Error
	y0	-0,49308	0,06842
	A1	2,75385	0,3916
B	t1	1046,54974	180,56472
	A2	18,83498	0,7106
	t2	144,81834	14,42169
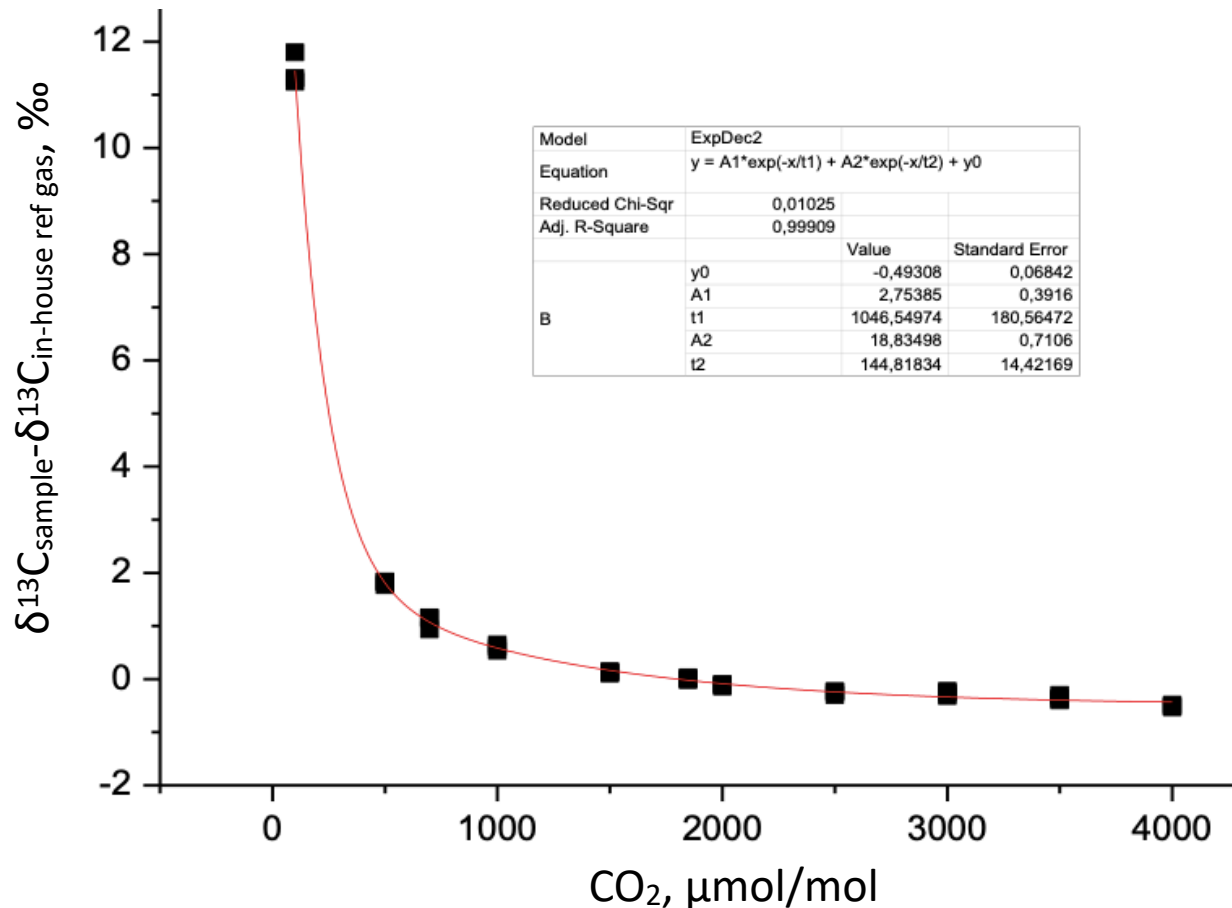
➠ Weights of references and sample should be chosen such as to get the same CO_2 signal at analyser

or correction should be performed
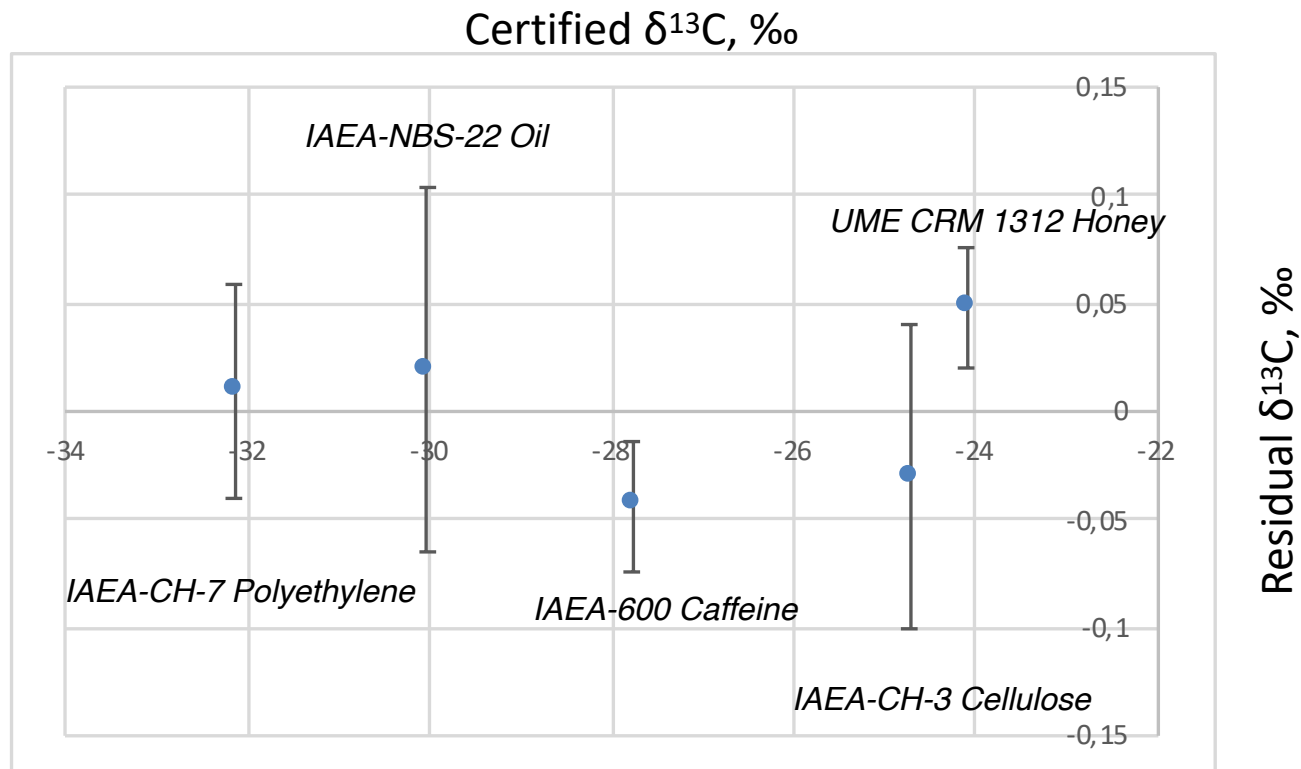
Results and discussion

CM-CRDS testing routine

▷ Linearity of CM-CRDS delta scale

Certified δ¹³C, ‰

$$y = 0.9856x - 0.3662$$

UME CRM 1312 Honey

IAEA-CH-3 Cellulose

IAEA-NBS-22 Oil   IAEA-600 Caffeine

IAEA-CH-7 Polyethylene

Measured δ¹³C, ‰

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Results and discussion

CM-CRDS testing routine

▷ Linearity of CM-CRDS delta scale

Certified δ^{13}C, ‰

➠ It doesn't look linear enough. Additional measurements with large number of CRMs will be performed

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Conclusion

To get more accurate measurements with CM-CRDS the following tests+ corrections should be performed periodically

▷ Background gases test+blank test+correction

▷ Stability (on-off test)+drift correction

▷ Linearity (peak size) test + concentration dependence correction + delta scale linearity test/correction