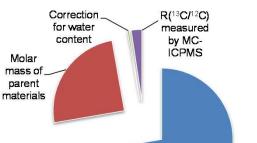
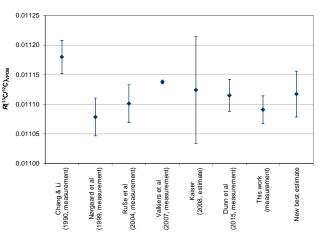
SI-traceable *n*(¹³C)/*n*(¹²C) isotope amount ratio measurements by IRMS and MC-ICPMS

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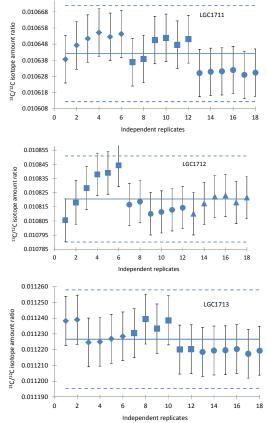
Comparability of ¹³C/¹²C **Study design** isotope ratios Production of Sourcing natural and glycine reference Variations in ¹³C/¹²C isotope ratios are commonly reported isotopically enriched material solutions as delta values (in ‰) on the international scale VPDBglycines $^{13}R_{sample}$ LSVEC: $\delta^{13}C_{VPDB} = -$ ¹³R_{VPDB} Concerns about comparability of $\delta^{(13)}$ values have been Homogeneity Stability raised due to replacement of one primary reference material by another and drifting of $\delta^{(13C)}$ values of the monitoring second primary reference material (LSVEC) during Certified storage $n(^{13}C)/n(^{12}C)$ isotope ratios Establishing traceability to the International System of Units (SI) is a sustainable solution ensuring accuracy and metrological traceability of measurement results. Calibrant Characterisation preparation To enable traceability to SI, new and improved methods of measurements by $n(^{13}C)/n(^{12}C)$ measurements by gas source isotope ratio MC-ICPMS mass spectrometry (IRMS) and multicollector inductively Confirmatory coupled plasma mass spectrometry (MC-ICPMS) have measurements by been developed at LGC. FIA-CO-IRMS **Traceability to SI units Preparation procedure for** calibrators of R(13C/12C) SI base unit: kilogram atic Parent isotopically enriched glycines were weighed and brought into solution and then mixed with each other in Metrological reference of measurement result SI coherent derived unit one per one (1/1) different proportions. Preparing system Material A Balance = Mettler-Toledo ¹³C isotope enriched glycine (¹³C₂H₅NO₂) XP205 Primary preparation glycine and eter = MC in the form of powder $(^{13}R = 211(2))$ ¹³C isotope enriched ctrome ICPMS; procedure for calibrators glycine Impurity measuring stems = ICP-MS, NMR Karl Fisher titration acquired from Sigma Aldrich Solution of material A in 2% HNO₃ Primary calibrators cally prepared from isotopically enriched glycine of kn Mixture 1 Mixture 2 Mixture 3 purity ¹³R = 0.009838(14) ¹³R = 1.01579(83) $^{13}R = 9.0176(69)$ Mixture 1, R = 0.009838(14); Measurement procedur Measuring system Mixture 2, R = 1.01579(83) Solution of material B in 2% HNO3 for MC-ICPMS ture 3. R = 9.0176(69) Material B ¹³C isotope depleted glycine (${}^{12}C_2H_5NO_2$) in the form of powder (${}^{13}R = 0.000237(2)$) Glycine solutions with certified ¹³C/¹²C isotope amount ratios Re-determination of R(¹³C/¹²C)_{VPDB} **Uncertainty budget**





Measurement results

 $n(^{13}C)/n(^{12}C)$ isotope ratios determined for the glycine CRM LGC171-KT in characterisation study. Uncertainty bars are U_c (*k*=1); solid and dotted lines are mean values and U_{exp} (*k*=2), respectively.



Certified values of absolute carbon isotope ratios and indicative $\delta^{13}C_{VPDB-LSVEC}$ values of LGC171-KT. Uncertainties in parentheses are U_{exp} (k=2).

Solution	n(¹³ C)/n(¹² C) ratio	$\delta^{\!\scriptscriptstyle 13}C_{\scriptscriptstyle VPDB-LSVEC}$ values, ‰
LGC1711	0.010642(30)	-42.22(0.34)
LGC1712	0.010821(30)	-24.66(0.24)
LGC1713	0.011227(32)	+12.55(0.22)

Conclusions

The developed methodology has been successfully applied to characterization of a new glycine reference material. Three glycine solutions of the CRM LGC171-KT produced in this study are intended for use in the calibration of instruments for the determination of absolute carbon isotope ratios.

Certified $R(^{13}C/^{12}C)$ values are traceable to the SI base units in the most direct way through calibration of the mass spectrometer with calibrators prepared from well



- Conservative uncertainty was assigned to molar mass values of parent glycines to account for potential presence of non-glycine forms of carbon.
- Homogeneity testing showed that both within and between bottle inhomogeneity are negligible.

Comparison of $R(^{13}C/^{12}C)_{VPDB}$ values previously reported in the literature together with a new best estimate. Error bars show the expanded uncertainties. characterised isotopically enriched glycines.

Improved measurement capabilities for isotope amount ratios $n({}^{13}C)/n({}^{12}C)$ have enabled provision of a new estimate of $R({}^{13}C/{}^{12}C)$ value of the zero-point of the VPDB isotope delta scale and a more reliable link between the relative carbon isotope delta scale and the SI.

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