A community-built calibration system: The case study of quantification of metabolites in grape juice by qNMR spectroscopy

Supplementary Data

Community-built calibration system: the case study of metabolites quantification in grape juice by qNMR spectroscopy

Biagia Musio[a*], Rosa Ragone[a,b], Stefano Todisco[a,b], Antonino Rizzuti,[a,b] Mario Latronico,[a,b] Piero Mastrorilli,[a,b] Stefania Pontrelli,[b] Nicola Intini,[b,c] Pasquale Scapicchio,[d,e] Maurizio Triggiani,[f] Tommaso Dinoia,[f] Domenico Acquotti,[g] Cristina Airoldi,[h] Michael Assfalg,[i] Alessandro Barge,[j] Francesca Benevelli,[k,l] Davide Bertelli,[m] Fabio Bertocchi,[n] Aurimas Bieliauskas,[o] Anna Borioni,[p] Augusta Caligiani,[q] Emanuela Callone,[r] Ales Čamra,[s] Flaminia Cesare Marincola,[t] Dinesh Chalasani,[u] Roberto Consonni,[v] Paolo Dambruoso,[w] Silvia Davalli,[x] Taylor David,[u] Bernd Diehl,[y] James Donarski,[z] Ana Gil,[aa] Roberto Gobetto,[ab] Luca Goldoni,[ac] Erwann Hamon,[ad] Andrea Kobrlová,[s] Francesco Longobardi,[ae] Renzo Luisi,[af] Denis Lynch,[ag] Domenico Mallamace,[ah] Stefano Mammi,[ai] Magali Martin-Biran,[aj] Pierluigi Mazzei,[ak,1] Andrea Mele,[al] Salvatore Milone,[am] Dolores Molero Vilchez,[an] Roger Mulder,[ao] Claudia Napoli,[k] Antonella Pepe,[ap] Daniele Ragno,[aq] Antonio Randazzo,[ar] Maria Cecilia Rossi,[m] Archimede Rotondo,[as,at] Algirdas Sackus,[o] Elena Sáez Barajas,[an] Elisabetta Schievano,[ai] Bhavaraju Sitaram,[u] Livio Stevanato,[j] Panteleimon G.Takis,[au] Jan Teipel,[av] Freddy Thomas,[aw] Elisabetta Torregiani,[ax] Daniela Valensin,[ay] Marina Veronesi,[ac] John Warren,[az] Julien Wist,[ba] Elina Zailer,[y] Cristiano Zuccaccia,[bb] Vito Gallo[a,b,d,**]

[a]Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica (DICATECh), Politecnico di Bari, via Orabona 4, I-70125, Bari, Italy

[b]Innovative Solutions S.r.l. – Spin Off del Politecnico di Bari, zona H 150/B, I-70015, Noci (BA), Italy

[c]Agenzia Regionale per la Prevenzione e la Protezione dell'Ambiente, ARPA Puglia, corso Trieste 127, I-70126, Bari, Italy

[d]SAMER (Special Agency of the Chamber of Commerce of Bari), via E. Mola 19, I-70121, Bari, Italy

[e]RETELAB (Italian network of the laboratories of the Chambers of Commerce) and LACHIMER (Special Agency of the Chamber of Commerce of Foggia), Via Manfredonia Km 2,200, I-71121 Foggia, Italy

[f]Dipartimento di Ingegneria Elettrica e dell'Informazione, Politecnico di Bari, via Orabona 4, I-70125, Bari, Italy

[g]Centro Inter-dipartimentale Misure (CIM), Università degli Studi di Parma, Parco Area delle Scienze 23/A, I-43124, Parma, Italy

[h]Dipartimento di Biotecnologie e Bioscienze, Università of Milano-Bicocca, P.zza della Scienza 2, I-20126, Milano, Italy

[i]Dipartimento di Biotecnologie, Università degli Studi di Verona, Cà Vignal 1, Strada le Grazie 15, I-37134, Verona, Italy

[j]Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, via Verdi 8, 10124, Torino, Italy

[k]Bruker Italia S.r.l., Viale V. Lancetti 43, I-20158, Milano, Italy

[l]7C-Consortium for NMR Research in Biotechnology and Material Science, Via Colombo 81, I-20133, Milano, Italy"

[m]Centro Interdipartimentale Grandi Strumenti (CIGS), Università di Modena e Reggio Emilia, via G. Campi 213/A, 41125 Modena, Italy

[n]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma “Tor Vergata”, via della Ricerca Scientifica, 00133 Roma, Italy
[o]Institute of Synthetic Chemistry, Kaunas University of Technology, K. Barsausko Str. 59, LT-51423, Kaunas, Lithuania
[p]Istituto Superiore di Sanità (ISS), Viale Regina Elena 299, I-00161, Roma, Italy
[q]Dipartimento di Scienze degli Alimenti e del Farmaco, Università degli Studi di Parma, Parco Area delle Scienze 23/A, I-43124, Parma, Italy
[r]Dipartimento di Ingegneria Industriale, via Sommarive 9, 38123 Povo (TN), Italy
[s]General Directorate of Customs, Budějovická 7, 140 00 Prague, Czech Republic
[t]Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria di Monserrato SS 554, I-09012 Monserrato (CA), Italy
[u]The United States Pharmacopeial Convention (USP), 12601 Twinbrook Parkway, Rockville, MD 20852-1790, USA
[v]Istituto per lo Studio delle Macromolecole del Consiglio Nazionale delle Ricerche, (ISMAC-CNR), Laboratorio NMR, Via Bassini 15, I-20133, Milano, Italy
[w]Istituto per la Sintesi Organica e la Fotoreattività del Consiglio Nazionale delle Ricerche (ISOF-CNR), via P. Gobetti 101, 40129 Bologna
[x]Aptuit (Verona) S.r.l., Via Fleming 4, I-37135, Verona, Italy
[y]Spectral Service AG, Emil-Hoffmann-Straße 33, 50996 Köln, Germany
[z]Fera Science Ltd, National Agri-Food Innovation Campus, Sand Hutton, York, YO41 1LZ, United Kingdom
[aa]CICECO - Aveiro Institute of Materials, Department of Chemistry, Technological Laboratories, University of Aveiro, 3810-093 Aveiro, Portugal
[ab]Dipartimento di Chimica, Università degli Studi di Torino, via Pietro Giuria 7, 10125 Torino, Italy
[ac]Fondazione Istituto Italiano di Tecnologia (IIT), via Morego 30, 16163 Genova, Italy
[ad]Aérial, 250 rue Laurent Fries - CS40443, 67412, Illkirch Cedex, France
[ae]Dipartimento di Chimica, Università degli Studi di Bari “A. Moro”, via Orabona 4, I-70125 Bari, Italy
[af]Department of Pharmacy – Drug Sciences, University of Bari “A. Moro”, FLAME-Lab – Flow Chemistry and Microreactor Technology Laboratory, Via E. Orabona 4, 70125 Bari, Italy
[ag]Analytical & Biological Chemistry Research Facility (ABCRF), University College Cork, Western Road, Cork City, Ireland
[ah]Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Viale F. Stagno d’Alcontres 31, I-98166 Messina, Italy
[ai]Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo 1, I-35100, Padova, Italy
[aj]Ctre Recherche Valorisation Application (CEREVAA), 12 Allée ISAAC NEWTON, 33650 MARTILLAC, France
[ak]Università di Napoli Federico II, Centro Interdipartimentale di Risonanza Magnetica Nucleare (CERMANU), via Università 100, 80055 Portici, Italy
[al]Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", via Mancinelli 7, 20131 Milano, Italy
[am]Istituto Zooprofilattico Sperimentale dell’Abruzzo e del Molise “G. Caporale” - Food Chemistry and Residues Unit, Campo Boario, I-64100 Teramo, Italy
[an]Universidad Complutense de Madrid, Avda. Complutense s/n Aulario Facultad de Quimicas, 28040, Madrid, Spain
[ao]Commonwealth Scientific and Industrial Research Organisation, Australian Government - CSIRO, Clayton South Vic 3169 Australia
[ap]Center for Cancer Research Hansen Life Sciences Research, Purdue University, 720 Clinic Drive, West Lafayette, IN 47907-2112, Indiana.
[aq]Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, via Fossato di Mortara 17, 44121 Ferrara, Italy

[ar]Dipartimento di Farmacia, Università di Napoli, via D. Montesano, 80131, Napoli, Italy
[as]Dipartimento di Scienze biomediche, odontoiatriche e delle immagini morfologiche e funzionali (BIOMORF), Università di Messina, Piazza Pugliatti 1, 98122 Messina, Italy.
[at]Science4life s.r.l., via Leonardo Sciascia Coop. Fede Pal.B, 98168 Messina, Italy
[au]Consorzio Interuniversitario Risonanze Magnetiche di Metallo Proteine – CERM/CIRMMP, via Luigi Sacconi 6, I-50019, Sesto Fiorentino (FI), Italy
[av]Chemical and Veterinary Investigation Agency of East-Westphalia-Lippe, Westerfeldstraße 1, 32758, Detmold, Germany
[aw]Eurofins Analytics France, 9 Rue P. A. Bobierre, BP42301, 44323, Nantes, France
[ax]Dipartimento di Scienze Chimiche, Università di Camerino, via S. Agostino 1, 62032, Camerino, Italy
[ay]Dipartimento di Biotecnologie, Chimica e Farmacia, via A. Moro 2, 53100 Siena, Italy
[az]LGC Limited, Queen's Road, TW11 0LY, Teddington, United Kingdom
[ba]Ciudadela Universitaria Melendez, Universidad del Valle Calle 13 No 100-00 Cali, Colombia
[bb]Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto 8, 06123 Perugia, Italia
[1]The present address is Dipartimento di Farmacia (DIFARMA), Università degli Studi di Salerno, 84084 Fisciano (SA), Italy

Sommario

Materials.

3-(Trimethylsilyl)-2,2,3,3-tetradeuteropropionic acid sodium salt (TSP, CAS N. 24493-21-8, 99 %D, Armar Chemicals, Döttingen, Switzerland), sodium azide (NaN_3, CAS N. 26628-22-8; ≥99.5%, Sigma-Aldrich, Milan, Italy), deuterium oxide (D_2O, CAS. N. 7789-20-0, 99.86 %D, Eurisotop, Saclay, France) and methanol-d_4 (CD_3OD, CAS. N. 811-98-3, 99.80 %D, Eurisotop, Saclay, France) were used for sample preparation. NMR tubes (Norell 509-UP 7) were provided by Norell, Landisville NJ, US. The NMR samples were prepared using the automated system for liquid handling (SamplePro Tube, Bruker BioSpin).

Wine grape samples (*cv*. Primitivo; Centro di Ricerca, Sperimentazione e Formazione in Agricoltura "Basile-Caramia (CRSFA), Locorotondo, Bari, Italy) were collected according to official recommendations (Regulations (CE) n. 834/2007, n. 889/2008, n. 1235/2008 and following modifications). 50 samples of *cv.* Primitivo were collected as follows: 30 berries were harvested randomly from different parts of the same plant for each sample. The samples were labelled according to the plant of origin, which was marked with a number and a letter, indicating respectively the vine-row and the sector of the vine-row to which the plant belonged. 1 bigger sample (1 Kg) was collected randomly from 3 plants belonging to the vineyard and labelled according to the same procedure. The samples were refrigerated at 4°C and transferred from the field to the laboratory, where they were stored at -20°C.

Experimental procedure.

The interlaboratory comparison was organized according to EN ISO/IEC 17043:2010 and reference normative therein (Conformity assessment - General requirements for proficiency testing) with 52 registered participants, 76 available spectrometers of which 65 producing results spectrometers [300, 400, 500, 600 and 700 MHz; Bruker (52), Agilent (9) and Jeol (4) manufacturers]. 75 sets of 8 NMR tubes were delivered to the participants and 65 spectrometers returned NMR data. The ILC participants were furnished with eight test NMR tubes, labelled as T, A, B, C, D, E, X, including a sample containing *cv.* Primitivo (tube X), and five test tubes (A – E) containing spiked solutions of four metabolites naturally contained in the grape juice (glucose, fructose, arginine and alanine). Tube T contained pure methanol-d_4 (CD_3OD, 99.80 %D) and was used as an NMR thermometer to calibrate the temperature of each spectrometer at 298.1 ± 0.1 K.(Findeisen et al. 2007) Tube X, containing aqueous solutions of wine grape juice (*cv*. Primitivo), was prepared as follows: 10 berries were defrosted at room temperature for 60 minutes. They were mechanically pressed and the resulting grape juice (~ 5 ml) was centrifuged (Ettich Rotofix 32A, 2500 g, 15 minutes). The supernatant (1.08 ml) was combined with a solution (84.6 mg / 50 ml) of NaN_3 in buffer [$(HC_2O_4)^-$/$(C_2O_4)_2^-$ 0.11 M, pH 4.2], giving Solution M1. 318 ml of this solution was combined stepwise with a volume of the buffer solution (222 ml) and a volume of a TSP/D_2O solution (60 mL, 0.10 g of TSP in 50 g of D_2O). To reach the final levels of metabolites concentrations in the tubes A, B, C, D and E (figure 2), portions of the solution M1 prepared on big scale for the preparation of tube X were combined opportunely with the following two mixtures of metabolites in the buffer [(HC_2O_4)-/$(C_2O_4)^{2-}$ 0.11 M, pH 4.2]: solution M2 was composed of glucose (8.3E-01 M), arginine

(1.43E-03 M), sodium malate (4.0E-02 M), sodium citrate (1.17E-03 M) and gamma aminobutyric acid (1.45E-04 10-3 M); solution M3 was composed of fructose (8.3E-02 M), tartaric acid (6.95E-04 M), alanine (1.68E-04 M) and threonine (1.26E-04 M).

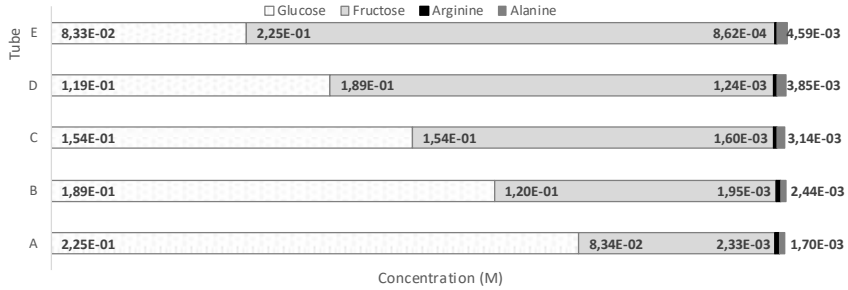


Figure S1. The final five levels of metabolites concentrations reached in the spiked solutions which are contained in tubes A – E.

Data acquisition and processing.

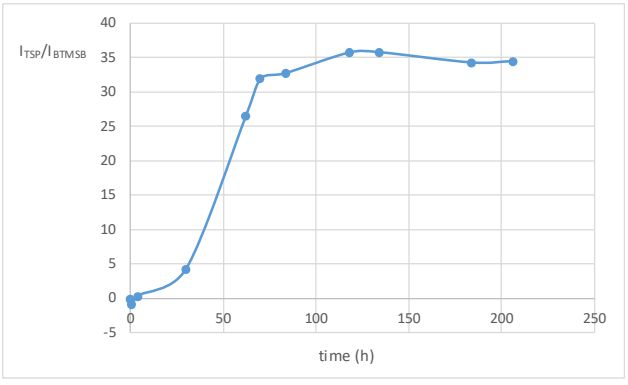
For each sample the participants were asked to perform five repetitions of a 1D 1H NOESY NMR experiment, preceded by a selective pre-saturation step to remove the residual water signal. The 5-fold replication was needed to comply with conditions for intermediate precision, i.e. same NMR tube, same spectrometer, same user, at least 24 h delay between runs, removal of the NMR tube from the magnet from run to run. The participants received experimental instructions for setting the acquisition parameters according to the spectrometer manufacturer requirements.

For Varian/Agilent spectrometers, guidelines included: pulse program (NOESY); size of fid (np, 128 K); spectral width (sw, 20 ppm); transmitter offset (tof): ca. 4.70 ppm (set the chemical shift value on the residual water signal); 90° hard pulse (pw, optimized by manual or automatic procedures keeping the pulse length as short as possible, preferably < 10 µs, if hardware allows it); steady state (ss, 8); number of transients (nt, 64); mixing time (mixN, 0.01 s); recycle delay (d1, 5 s); no sspul (sspul = 'n'); no ZQ filter (Gzqfilt = 'n'); no homo spoil during mixing time (gt1 = 0, gzlvl1 = 0 and gstab = 0); presaturation during the whole length of d1, centered at the HDO residual signal with a nutation frequency of about 25 Hz [satmode = 'yn', satdly = d1, satfrq = tof; satpwr should be set to yield r1 of about 25 after running the command getpower(satpwr,tn):r1]; receiver gain optimization (once optimized for tube A, use the obtained receiver gain value also for all replicates and for all tubes A – E, X).

For Bruker spectrometers, guidelines included: pulse program: noesypr1d; size of FID (TD, 128 K); spectral width (SW, 20 ppm); transmitter offset, ca. 4.70 ppm (set at the chemical shift value of the residual water signal); 90° hard pulse (p1, optimized by manual or automatic procedures keeping the pulse length as short as possible, preferably < 10 µs, if hardware allows it); power level for presaturation (pl9, calculated by command "pulse 25Hz" after optimization of p1); dummy scans (ds, 8); number of scans (ns, 64); mixing time (d8, 0.01 s); recycle delay (d1, 5 s); receiver gain optimization (once optimized for tube A, use the obtained receiver gain value also for all replicates and for all tubes A – E, X).

For Jeol spectrometers, guidelines included: pulse program: noesy_abs; y_points = 1; size of fid (x_point = 131072); spectral width (x_sweep = 20); transmitter offset (x_offset = 4.7); 90º hard pulse (x_pulse = x90; x_atn = xatn) to be optimized by manual or automatic procedures, keeping pulse length as short as possible, preferably < 10 µs; steady state (x_prescans = 8); number of transients (scans = 64); mixing time (mix_time = 0.01); recycle delay (relaxation_delay = 5); presaturation during the whole length of recycle delay, centered at the HDO residual signal with a γB2 power of about 25 Hz (irr_mode = presaturation; irr-offset = x_offset; presat_time_flag = y); use the following formula to calculate the value of irr_attenuator corresponding to 25 Hz: irr_attenuation = x_atn + 20log(10.000/x90); receiver gain optimization (once optimized for tube A, use the obtained receiver gain value also for all replicates and for all tubes B-E, X and Y). The NMR raw data sets (FIDs and signal integrals) were uploaded by each laboratory on the website http://nmr.mxcs.it/index.php developed according to internationally agreed procedures. The NMR spectra could be re-processed Topspin 1.3 - AMIX 3.9.9 (Bruker BioSpin GmbH, Germany) and Mnova (Mestrelab Research, Spain). FID was zero-filled with 128 K number of points. FIDs were extended by zero-filling to a final size of 256 K. Fourier transformation was performed by applying an exponential multiplication function with a line broadening of 0.1 Hz. Users could choose to apply either manual or automatic procedures for the phase and the baseline correction (without any limitations provided that the same procedure is applied to all NMR spectra). The calculation of peak area was the only procedure accepted for the signal integration. The TSP singlet signal (0.00 ppm) was used as internal reference compound, upon ascertaining it was stable in solution over the time four days after the sample preparation. The integral of TSP signal was referred to the integral of 1,4-bis(trimethylsilyl)benzene (BTMSB) used as external reference compound (2.08 mg of BTMSB in 620 µl of 1,1,2,2-tetrachloroethane-d_2).

time (h)	TSP	BTMSB	TSP/BTMSB
0	22865957,19	106502671	0,214698439
1	22692030	106662826,6	0,21274544
4	22349555,94	103727159,1	0,215464842
30	23446407,44	104751304,1	0,223829265
62	29709773,94	109437063,6	0,271478172
70	32117033,31	113384010,6	0,283258928
84	31644292,5	110999759,7	0,285084333
118	31888216,56	109401903,1	0,291477713
134	31874377,06	109292721,7	0,291642266
184	30892070,75	107131325,4	0,288357029
206	30679005,31	106215720,6	0,288836767



Selection of spectra regions for signals integration

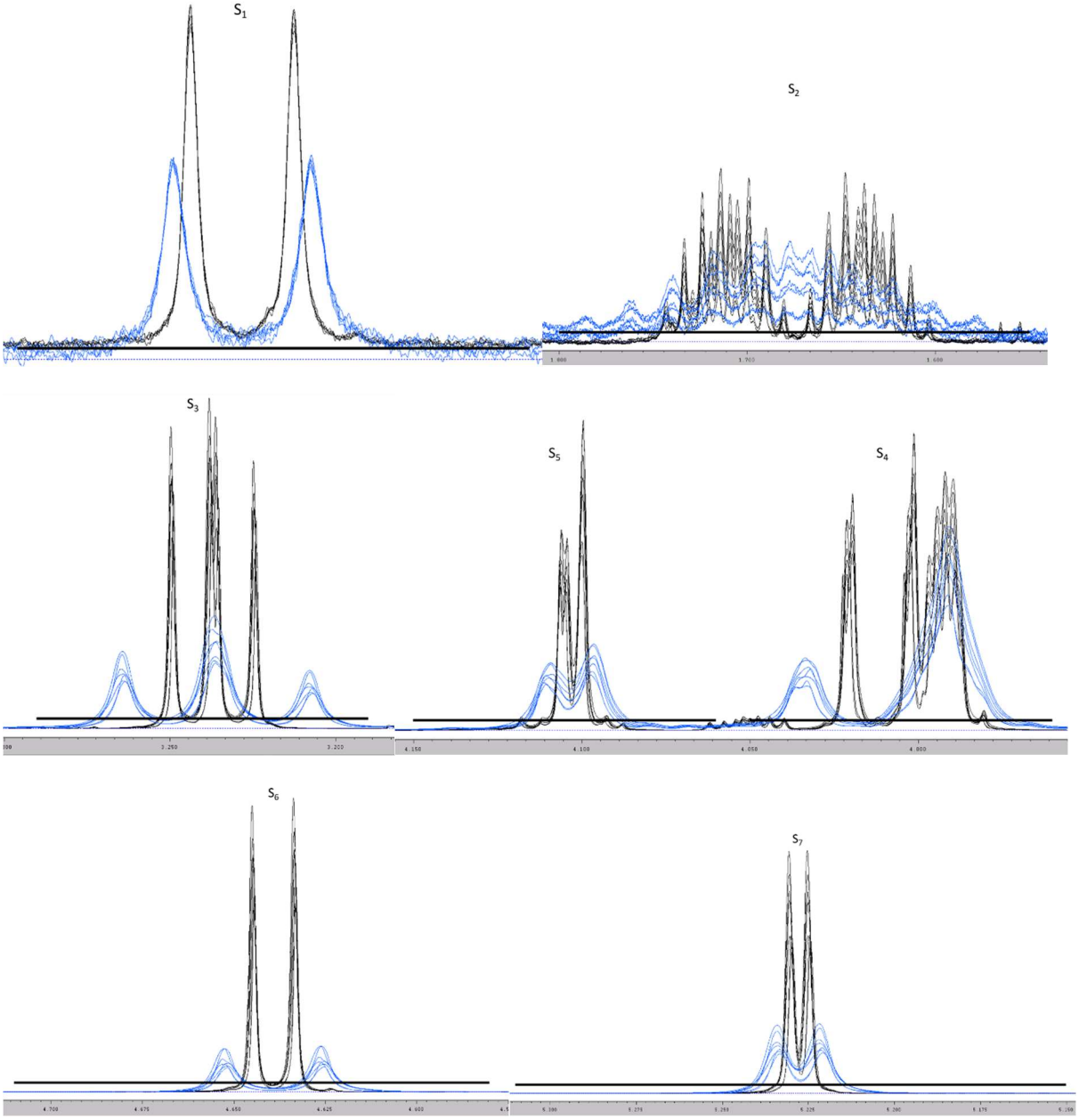


Figure S2. The regions of the spectra which were selected and integrated. For convenience are represented only the spectra of tubes A – E recorded by a 300 MHz spectrometer (blue spectra) and a 700 MHz spectrometer (black spectra).

Application of ANOVA to test the linearity of the regression curves

- Example 1 (Laboratory 11 during the analysis of signal 1): accepted regression curve with P-value of F lower than alpha value (0.05).

Statistic of regression	
Multiple R	0.999090052
R Square	0.998180932
Adjusted R Square	0.998115965
Standard Error	0.018349051
Observations	30

ANOVA

	gdl	*SQ*	*MQ*	*F (1-tail test)*	*P-value of F*	*Alpha*	*Linearity*
Regression	1	5.173036323	5.173036	15364.49595	6.49739E-40	0.05	accepted regression
Residual	28	0.009427255	0.000337				
Total	29	5.182463577					

- Example 2 (Laboratory 42 during the analysis of signal 1): rejected regression curve with P-value of F higher than alpha value (0.05).

Statistic of Regression	
Multiple R	0.219099
R Square	0.048004
Adjusted R Square	0.014005
Standard Error	2.946559
Observations	30

ANOVA

	gdl	*SQ*	*MQ*	*F (1-tail test)*	*P-value of F*	*Alpha*	*Linearity*
Regression	1	12.25844	12.25844	1.411902929	0.244722052	0.05	rejected regression
Residual	28	243.1019	8.68221				
Total	29	255.3603					

Application of ANCOVA to test the parallelism and the coincidence of the calibration curves with respect to the reference regression curve

The ANCOVA (ANalysis of COVAriance) method was applied to test the parallelism of each selected line with respect to the *community-built reference line*. As an example, in figure S3 is represented the application of this approach to the case of the regression line produced by the spectrometer of laboratory 11 (red line) and the *reference line* (black dashed line). The average residual of the regression line of the spectrometer 11 and the reference regression line was calculated as [$MS_{Pooled} = (RSS_{Lab11} + RSS_{Ref})/df$], where the MS_{Pooled} is the average Mean Square error of all the involved curves, RSS_{Lab11} and RSS_{Ref} are the residual sum of square of the regression line of the spectrometer 11 and of the reference regression line, respectively, and *df* is the degree of freedom calculated as n – 2 (n = number of observations). A common regression line (yellow line, figure 4) was designed using the overall variables of the reference line and the regression line under analysis and an MS_{common} was calculated (see supporting material for further details). The average residual of the slopes was calculated as [$MS_{Slopes} = (RSS_{common} – RSS_{Pooled})/df$] where *df* is calculated, in this case, as n–1 (n = number of lines which are compared). Next, the probability density for the one-tail F-distribution of the positive ratio F (calculated as [$F = MS_{Regression\ Coefficient}/MS_{Pooled}$], when $MS_{Slopes} > MS_{Pooled}$, or as [$F = MS_{Pooled}/MS_{Slopes}$] when $MS_{Slopes}<MS_{Pooled}$ and representing the degree of diversity between MS_{Pooled} and MS_{Slopes}) was evaluated. Only the lines for which such test gave a probability higher than the alpha-value (0.025) defined as a threshold were considered parallel and admitted to the following step testing the coincidence of the *y*-intercept. A similar approach as described for T4 – parallelism test was used in T5 – coincidence test. For this purpose, the degree of freedom of the common regression model was increased of one unit, giving a new regression model which was called total. Then, the $MS_{y\text{-intercept}}$, which represented the average difference in the *y*-intercepts between the line under investigation and the *community-built reference line*, was calculated as [$(RSS_{total}–RSS_{common})/df$], where *df* was given by n–1 (n = number of lines which are compared). Analogously to the parallelism test, the probability density for the one-tail F-distribution of F was evaluated (T5 – coincidence) for the remaining 34 regression lines. In this case, F was calculated as either $F=MS_{y\text{-intercept}}/MS_{Common}$, when $MS_{y\text{-intercept}}>MS_{Common}$, or $F=MS_{Common}/MS_{y\text{-intercept}}$, when $MS_{y\text{-intercept}}<MS_{Common}$. Only the lines for which such test gave a probability higher than the alpha-value (0.025) defined as a threshold were considered coincident (see supporting material for further details).

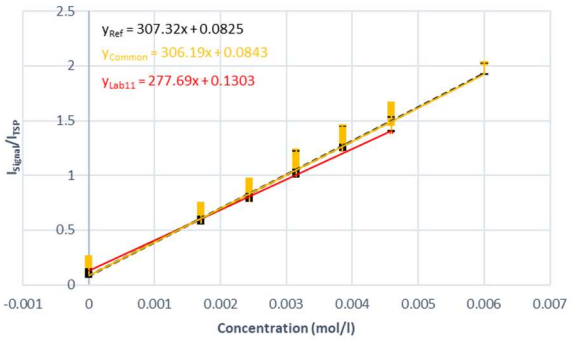


Figure S3. Application of the consecutive tests verifying the coincidence of the slopes and the elevations between the regression line produced by the spectrometer 11 and the reference line designed using all the data produced by the laboratories which were preliminarily assessed as suitable for analyte quantification. The common line (yellow line) represents the line designed using both the variables of the reference line (black dashed line) and the line under quality assessment (red line).

- Example: Laboratory 11 during the analysis of signal 1.

Observations	X	Y
1	0.001699674	0.60050798
2	0.001699674	0.59621622
3	0.001699674	0.59736326
4	0.001699674	0.6
5	0.001699674	0.59960763
6	0.0024362	0.78852682
7	0.0024362	0.79344486
8	0.0024362	0.79406751
9	0.0024362	0.79213293
10	0.0024362	0.78876329
11	0.003144398	1.01577238
12	0.003144398	1.02876002
13	0.003144398	1.02214598
14	0.003144398	1.02431754
15	0.003144398	1.01668486
16	0.003852596	1.21366794
17	0.003852596	1.2313476
18	0.003852596	1.22362385
19	0.003852596	1.22827497
20	0.003852596	1.23001443
21	0.004589121	1.37900753
22	0.004589121	1.37638427
23	0.004589121	1.38662589
24	0.004589121	1.3836296
25	0.004589121	1.37730943
26	0	0.1327818
27	0	0.13177891
28	0	0.12871597
29	0	0.12895479
30	0	0.12795564

	Identification	n (observations)	SX	SY	SX^2	SY^2	SXY	Mean X	Mean Y
1	Laboratory 11	30	0.078609945	25.73838	0.000273	27.26461	0.086072	0.002620332	0.85794613
2	Reference curve	1620	4.24493703	1434.182	0.014746	1611.8773	4.867452	0.002620332	0.88529768
	number of curves	2							
	Total	1650	4.323546975	1459.921	0.015019	1639.1419	4.953524		

ANCOVA

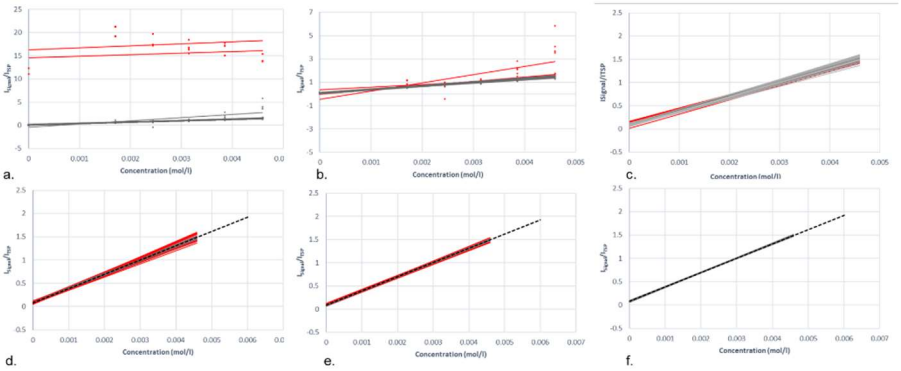
		df	SdX2	SdXdY	SdY2	slope (b)	Residual SS	MS	*y* -Intercept
1	Laboratory 11	28	6.70845E-05	0.018629	5.182464	277.69086	0.009427	0.000336688	0.13030403
2	Reference curve	1618	0.003622564	1.109419	342.1991	306.25243	2.436786	0.001506048	0.08281479
	Pooled curve	1646					2.446214	0.001486156	
	Reg. Coef.	1					0.05373	0.053730099	
	Common	1647	0.003689649	1.128048	347.3816	305.73313	2.499944	0.001517877	
	Adj. Means	1					0.022035	0.022035162	
	Total	1648	0.003689649	1.128048	347.4036	305.73313	2.521979	0.001530327	

	F (2-tails test)	numerator df	denominator df	P	Alpha	**Decision**
H0: Slopes equal	36.15372964	1	1646	2.242E-09	0.025	Not Parallel
H0: Elevations equal	14.51709174	1	1647	0.000144	0.025	Not Coincident

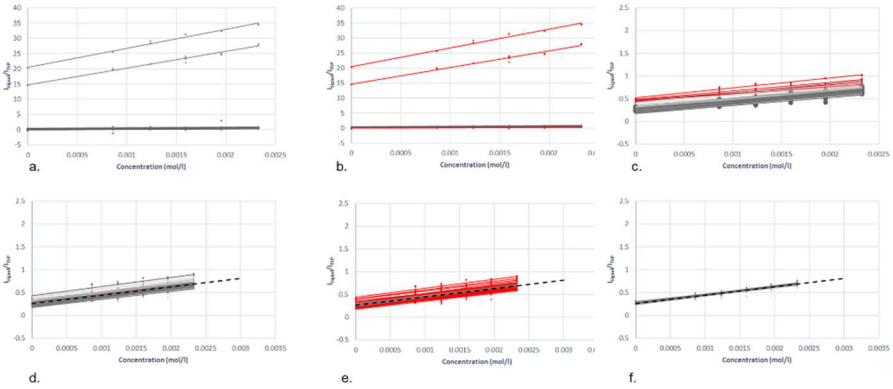
Selection of the regression curves produced by the ILC participants.

Plots of the regression curves produced for the signals 1 - 7 during the sequence of selection tests. a. linearity test; b. Huber and Cochran tests on slopes; c. Huber and Cochran tests on intercepts; d. parallelism test on slopes; e. coincidence tests on elevations; f. final suitable regression lines for quantification purposes. Black curves passed successfully the selection test; red lines failed the selection test; black dashed line represents the reference regression curve.

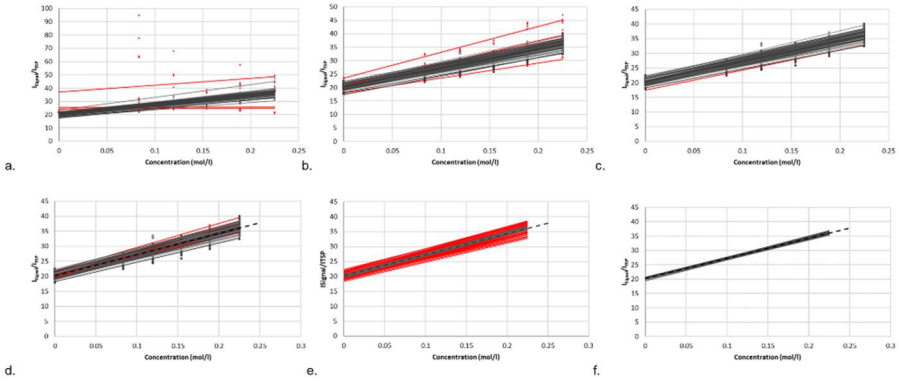
Signal S1 [1.42, 1.51 ppm]: alanine



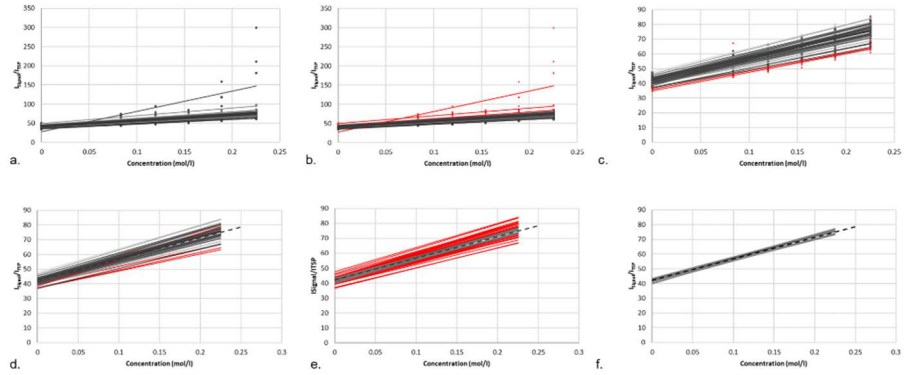
Signal S2 [1.55, 1.80 ppm]: arginine



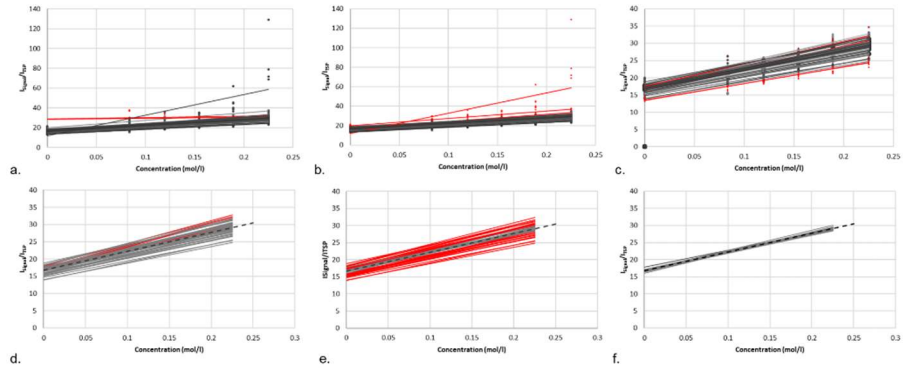
Signal S3 [3.19, 3.29 ppm]: glucose



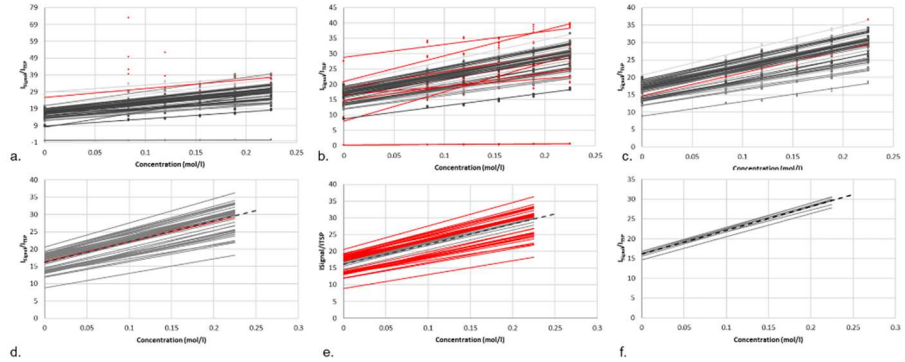
Signal S4 [3.96, 4.05 ppm]: fructose



Signal S5 [4.06, 4.15 ppm]: fructose



Signal S6 [4.58, 4.71 ppm]: glucose



Signal S7 [5.15, 5.31 ppm]: glucose

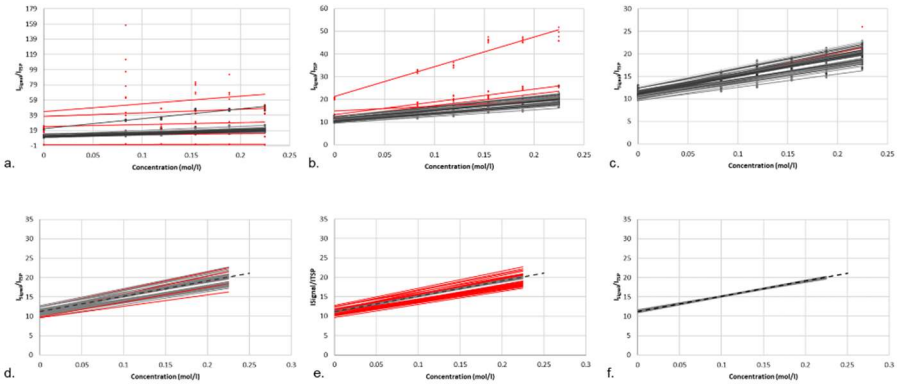


Table S1. qNMR analysis of alanine (S1)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of alanine (S1 at 1.42 - 1.51 ppm).

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y*-intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	outlier	outlier	outlier
2	Varian 500, 2002	OK	OK	OK	OK	OK
3	Varian 700, 2005	OK	OK	OK	outlier	outlier
4	Bruker 600, 2006	OK	OK	OK	outlier	outlier
5	Bruker 600, 2007	OK	OK	OK	OK	outlier
6	Bruker 500, 2016	OK	OK	OK	outlier	outlier
7	Bruker 400, 2002	OK	OK	OK	outlier	outlier
8	Bruker 500, 2014	OK	OK	OK	OK	outlier
9	Bruker 400, 2010	OK	OK	OK	outlier	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	OK
11	Bruker 400, 2013	OK	OK	OK	outlier	outlier
12	Bruker 500, 2016	OK	OK	OK	OK	OK
13	Bruker 600, 1999	OK	OK	OK	OK	OK
14	Bruker 600, 2007	OK	OK	OK	OK	OK
15	Bruker 600, 2014	OK	OK	OK	OK	OK
16	Bruker 400, 2003	OK	OK	OK	OK	OK
17	Bruker 600, 2014	OK	OK	OK	OK	outlier
18	Bruker 600, 2014	OK	OK	OK	outlier	outlier
19	Bruker 600, 2009	OK	OK	OK	OK	outlier
20	Bruker 400, 2010	OK	OK	outlier	outlier	outlier
21	Bruker 600, 1998	OK	OK	OK	outlier	outlier
22	Bruker 400, 2014	OK	OK	OK	OK	OK
23	Bruker 700, 2010	OK	OK	OK	outlier	outlier
24	Bruker 500, 1987	OK	OK	OK	OK	OK
25	Bruker 400, 2003	OK	OK	outlier	outlier	outlier
26	Bruker 600, 2006	OK	outlier	outlier	outlier	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	outlier	outlier	outlier	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	OK
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	OK	OK
32	Bruker 500, 2001	OK	OK	OK	OK	OK
33	Bruker 400, 2000	OK	OK	OK	outlier	outlier
34	Agilent 500, 2008	OK	OK	OK	OK	outlier
35	Bruker 400, 2009	OK	OK	OK	OK	OK
36	Bruker 600, 1991	OK	OK	OK	OK	OK
37	Bruker 500, 2014	OK	OK	OK	OK	outlier
38	Varian 400, 1997	OK	OK	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	OK
40	Agilent 500, 2014	OK	OK	OK	OK	OK
41	Bruker 500, 2004	OK	OK	OK	OK	OK
42	Bruker 700, 2001	outlier	outlier	outlier	outlier	outlier
43	Bruker 400, 2015	OK	OK	OK	outlier	outlier
44	Jeol 600, 2016	OK	OK	OK	outlier	outlier
45	Bruker 600, 2007	OK	OK	OK	outlier	outlier
46	Bruker 500, 2014	OK	OK	OK	OK	outlier
47	Bruker 500, 2014	OK	OK	OK	outlier	outlier
48	Bruker 400, 2005	outlier	outlier	outlier	outlier	outlier
49	Bruker 500, 2017	OK	OK	OK	OK	OK
50	Bruker 400, 2016	OK	OK	OK	OK	OK
51	Bruker 500, 2010	OK	OK	OK	outlier	outlier
52	Bruker 400, 2011	OK	OK	OK	outlier	outlier
53	Agilent 500, 2015	OK	OK	OK	OK	OK
54	Bruker 400, 2016	OK	OK	OK	OK	outlier
55	Bruker 500, 2004	OK	OK	OK	OK	OK
56	Bruker 700, 2013	OK	OK	OK	outlier	outlier
57	Bruker 400, 2012	OK	OK	outlier	outlier	outlier
58	Varian 400, 2013	OK	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	OK	OK
60	Jeol 600, 2016	OK	OK	OK	OK	outlier
61	Bruker 300, 2001	OK	OK	OK	outlier	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	OK
63	Jeol 600, 2016	OK	OK	OK	OK	OK
64	Jeol 300, 2000	OK	OK	OK	outlier	outlier
65	Bruker 400, 2012	OK	OK	OK	outlier	outlier
	n	63	59	54	34	25

Table S2. qNMR analysis of arginine (S2)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of arginine (S2 at 1.55 - 1.80 ppm.

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y* -intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	OK	OK	outlier
2	Varian 500, 2002	OK	OK	OK	OK	OK
3	Varian 700, 2005	OK	OK	OK	OK	OK
4	Bruker 600, 2006	OK	OK	OK	OK	OK
5	Bruker 600, 2007	OK	OK	OK	OK	OK
6	Bruker 500, 2016	OK	OK	OK	OK	outlier
7	Bruker 400, 2002	OK	OK	OK	OK	outlier
8	Bruker 500, 2014	OK	OK	OK	OK	outlier
9	Bruker 400, 2010	OK	OK	OK	OK	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	OK
11	Bruker 400, 2013	OK	OK	OK	OK	outlier
12	Bruker 500, 2016	OK	OK	OK	OK	OK
13	Bruker 600, 1999	OK	OK	OK	OK	outlier
14	Bruker 600, 2007	OK	OK	OK	OK	outlier
15	Bruker 600, 2014	OK	OK	OK	OK	outlier
16	Bruker 400, 2003	OK	OK	OK	OK	outlier
17	Bruker 600, 2014	OK	outlier	outlier	outlier	outlier
18	Bruker 600, 2014	OK	OK	OK	OK	outlier
19	Bruker 600, 2009	OK	OK	OK	OK	outlier
20	Bruker 400, 2010	OK	OK	outlier	outlier	outlier
21	Bruker 600, 1998	OK	OK	OK	OK	OK
22	Bruker 400, 2014	OK	OK	OK	OK	outlier
23	Bruker 700, 2010	OK	OK	OK	OK	outlier
24	Bruker 500, 1987	OK	OK	OK	OK	OK
25	Bruker 400, 2003	OK	OK	outlier	outlier	outlier
26	Bruker 600, 2006	OK	OK	OK	OK	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	OK	outlier	outlier	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	outlier
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	OK	outlier
32	Bruker 500, 2001	OK	OK	OK	OK	OK
33	Bruker 400, 2000	OK	OK	OK	OK	outlier
34	Agilent 500, 2008	OK	OK	outlier	outlier	outlier
35	Bruker 400, 2009	OK	OK	OK	OK	OK
36	Bruker 600, 1991	OK	OK	OK	OK	outlier
37	Bruker 500, 2014	OK	OK	OK	OK	outlier
38	Varian 400, 1997	OK	outlier	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	OK
40	Agilent 500, 2014	OK	outlier	outlier	outlier	outlier
41	Bruker 500, 2004	OK	OK	OK	OK	OK
42	Bruker 700, 2001	OK	outlier	outlier	outlier	outlier
43	Bruker 400, 2015	OK	OK	OK	OK	OK
44	Jeol 600, 2016	OK	outlier	outlier	outlier	outlier
45	Bruker 600, 2007	OK	OK	OK	OK	OK
46	Bruker 500, 2014	OK	OK	OK	OK	outlier
47	Bruker 500, 2014	OK	OK	OK	OK	outlier
48	Bruker 400, 2005	OK	outlier	outlier	outlier	outlier
49	Bruker 500, 2017	OK	OK	OK	OK	outlier
50	Bruker 400, 2016	OK	OK	OK	OK	outlier
51	Bruker 500, 2010	OK	OK	OK	OK	OK
52	Bruker 400, 2011	OK	outlier	outlier	outlier	outlier
53	Agilent 500, 2015	OK	OK	OK	OK	OK
54	Bruker 400, 2016	OK	OK	OK	OK	outlier
55	Bruker 500, 2004	OK	OK	OK	OK	OK
56	Bruker 700, 2013	OK	outlier	outlier	outlier	outlier
57	Bruker 400, 2012	OK	outlier	outlier	outlier	outlier
58	Varian 400, 2013	OK	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	OK	OK
60	Jeol 600, 2016	OK	OK	OK	OK	outlier
61	Bruker 300, 2001	OK	OK	OK	OK	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	outlier
63	Jeol 600, 2016	OK	OK	OK	OK	OK
64	Jeol 300, 2000	OK	outlier	outlier	outlier	outlier
65	Bruker 400, 2012	OK	OK	OK	OK	outlier
	n	65	53	49	49	20

Table S3. qNMR analysis of glucose (S3)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of glucose (S3 at 3.19 - 3.29 ppm).

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y* -intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	OK	OK	outlier
2	Varian 500, 2002	OK	OK	OK	OK	outlier
3	Varian 700, 2005	OK	OK	OK	OK	outlier
4	Bruker 600, 2006	OK	OK	OK	OK	outlier
5	Bruker 600, 2007	OK	OK	OK	OK	outlier
6	Bruker 500, 2016	OK	OK	OK	OK	outlier
7	Bruker 400, 2002	OK	OK	OK	OK	outlier
8	Bruker 500, 2014	OK	OK	OK	outlier	outlier
9	Bruker 400, 2010	OK	OK	OK	OK	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	outlier
11	Bruker 400, 2013	OK	OK	OK	OK	outlier
12	Bruker 500, 2016	OK	OK	OK	OK	OK
13	Bruker 600, 1999	OK	OK	OK	OK	outlier
14	Bruker 600, 2007	OK	OK	OK	OK	OK
15	Bruker 600, 2014	OK	OK	OK	OK	OK
16	Bruker 400, 2003	OK	OK	OK	OK	outlier
17	Bruker 600, 2014	OK	OK	OK	OK	outlier
18	Bruker 600, 2014	OK	OK	OK	OK	outlier
19	Bruker 600, 2009	OK	OK	OK	OK	OK
20	Bruker 400, 2010	OK	OK	OK	OK	outlier
21	Bruker 600, 1998	OK	OK	OK	OK	OK
22	Bruker 400, 2014	OK	OK	OK	OK	outlier
23	Bruker 700, 2010	OK	OK	OK	outlier	outlier
24	Bruker 500, 1987	OK	OK	OK	OK	OK
25	Bruker 400, 2003	OK	OK	OK	OK	outlier
26	Bruker 600, 2006	OK	OK	OK	OK	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	outlier	outlier	outlier	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	outlier
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	outlier	outlier
32	Bruker 500, 2001	OK	OK	OK	OK	outlier
33	Bruker 400, 2000	OK	OK	OK	OK	outlier
34	Agilent 500, 2008	OK	OK	OK	OK	outlier
35	Bruker 400, 2009	OK	OK	OK	OK	OK
36	Bruker 600, 1991	OK	OK	OK	OK	OK
37	Bruker 500, 2014	OK	OK	OK	OK	outlier
38	Varian 400, 1997	OK	outlier	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	outlier
40	Agilent 500, 2014	OK	OK	OK	OK	OK
41	Bruker 500, 2004	OK	OK	OK	OK	outlier
42	Bruker 700, 2001	outlier	outlier	outlier	outlier	outlier
43	Bruker 400, 2015	OK	OK	OK	OK	outlier
44	Jeol 600, 2016	OK	OK	OK	OK	outlier
45	Bruker 600, 2007	OK	OK	OK	OK	OK
46	Bruker 500, 2014	OK	OK	OK	OK	outlier
47	Bruker 500, 2014	OK	OK	OK	OK	outlier
48	Bruker 400, 2005	outlier	outlier	outlier	outlier	outlier
49	Bruker 500, 2017	OK	OK	OK	outlier	outlier
50	Bruker 400, 2016	OK	OK	OK	OK	outlier
51	Bruker 500, 2010	OK	OK	OK	OK	OK
52	Bruker 400, 2011	OK	OK	OK	OK	outlier
53	Agilent 500, 2015	OK	OK	OK	OK	OK
54	Bruker 400, 2016	OK	OK	OK	outlier	outlier
55	Bruker 500, 2004	OK	OK	OK	OK	OK
56	Bruker 700, 2013	OK	OK	OK	OK	outlier
57	Bruker 400, 2012	OK	OK	OK	OK	OK
58	Varian 400, 2013	outlier	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	outlier	outlier
60	Jeol 600, 2016	OK	OK	OK	OK	outlier
61	Bruker 300, 2001	OK	OK	outlier	outlier	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	OK
63	Jeol 600, 2016	OK	OK	OK	OK	OK
64	Jeol 300, 2000	OK	OK	OK	OK	outlier
65	Bruker 400, 2012	OK	OK	OK	OK	outlier
	n	62	59	58	52	17

Table S4. qNMR analysis of fructose (S4)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of fructose (S4 at 3.96 - 4.05 ppm).

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y*-intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	OK	OK	outlier
2	Varian 500, 2002	OK	OK	OK	OK	outlier
3	Varian 700, 2005	OK	OK	OK	OK	outlier
4	Bruker 600, 2006	OK	OK	OK	OK	outlier
5	Bruker 600, 2007	OK	OK	OK	OK	outlier
6	Bruker 500, 2016	OK	OK	OK	OK	OK
7	Bruker 400, 2002	OK	OK	OK	OK	outlier
8	Bruker 500, 2014	OK	OK	OK	OK	OK
9	Bruker 400, 2010	OK	OK	OK	OK	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	outlier
11	Bruker 400, 2013	OK	OK	OK	outlier	outlier
12	Bruker 500, 2016	OK	OK	OK	OK	OK
13	Bruker 600, 1999	OK	OK	OK	OK	outlier
14	Bruker 600, 2007	OK	OK	OK	OK	outlier
15	Bruker 600, 2014	OK	OK	OK	OK	OK
16	Bruker 400, 2003	OK	OK	OK	OK	OK
17	Bruker 600, 2014	OK	OK	OK	OK	outlier
18	Bruker 600, 2014	OK	OK	OK	outlier	outlier
19	Bruker 600, 2009	OK	OK	OK	OK	outlier
20	Bruker 400, 2010	OK	OK	OK	OK	outlier
21	Bruker 600, 1998	OK	OK	OK	OK	OK
22	Bruker 400, 2014	OK	OK	OK	OK	outlier
23	Bruker 700, 2010	OK	OK	OK	OK	outlier
24	Bruker 500, 1987	OK	OK	OK	OK	OK
25	Bruker 400, 2003	OK	OK	OK	OK	outlier
26	Bruker 600, 2006	OK	outlier	outlier	outlier	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	OK	OK	outlier	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	outlier
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	OK	outlier
32	Bruker 500, 2001	OK	OK	OK	OK	OK
33	Bruker 400, 2000	OK	OK	OK	OK	outlier
34	Agilent 500, 2008	OK	OK	OK	OK	OK
35	Bruker 400, 2009	OK	OK	OK	OK	OK
36	Bruker 600, 1991	OK	OK	OK	OK	OK
37	Bruker 500, 2014	OK	OK	OK	outlier	outlier
38	Varian 400, 1997	OK	OK	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	outlier
40	Agilent 500, 2014	OK	OK	OK	OK	outlier
41	Bruker 500, 2004	OK	OK	OK	OK	outlier
42	Bruker 700, 2001	OK	OK	OK	OK	outlier
43	Bruker 400, 2015	OK	OK	OK	OK	outlier
44	Jeol 600, 2016	OK	OK	OK	OK	OK
45	Bruker 600, 2007	OK	OK	OK	OK	outlier
46	Bruker 500, 2014	OK	OK	OK	OK	outlier
47	Bruker 500, 2014	OK	OK	OK	OK	outlier
48	Bruker 400, 2005	OK	OK	OK	OK	OK
49	Bruker 500, 2017	OK	OK	OK	OK	outlier
50	Bruker 400, 2016	OK	OK	OK	outlier	outlier
51	Bruker 500, 2010	OK	OK	OK	OK	outlier
52	Bruker 400, 2011	OK	OK	OK	OK	outlier
53	Agilent 500, 2015	OK	OK	OK	OK	OK
54	Bruker 400, 2016	OK	OK	OK	OK	OK
55	Bruker 500, 2004	OK	OK	OK	OK	OK
56	Bruker 700, 2013	OK	OK	OK	OK	outlier
57	Bruker 400, 2012	OK	OK	OK	OK	OK
58	Varian 400, 2013	OK	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	OK	OK
60	Jeol 600, 2016	OK	OK	OK	OK	outlier
61	Bruker 300, 2001	OK	OK	outlier	outlier	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	OK
63	Jeol 600, 2016	OK	OK	OK	OK	OK
64	Jeol 300, 2000	OK	OK	outlier	outlier	outlier
65	Bruker 400, 2012	OK	OK	OK	OK	OK
	n	65	62	59	54	22

Table S5. qNMR analysis of fructose (S5)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of fructose (S5 at 4.06 - 4.15 ppm).

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y* -intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	OK	OK	outlier
2	Varian 500, 2002	OK	OK	OK	OK	outlier
3	Varian 700, 2005	OK	OK	OK	OK	outlier
4	Bruker 600, 2006	OK	OK	OK	OK	outlier
5	Bruker 600, 2007	OK	OK	OK	OK	OK
6	Bruker 500, 2016	OK	OK	OK	OK	outlier
7	Bruker 400, 2002	OK	OK	OK	OK	outlier
8	Bruker 500, 2014	OK	OK	OK	OK	OK
9	Bruker 400, 2010	OK	OK	OK	OK	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	outlier
11	Bruker 400, 2013	OK	OK	OK	OK	outlier
12	Bruker 500, 2016	OK	OK	OK	OK	outlier
13	Bruker 600, 1999	OK	OK	OK	OK	outlier
14	Bruker 600, 2007	OK	OK	OK	outlier	outlier
15	Bruker 600, 2014	OK	OK	OK	OK	outlier
16	Bruker 400, 2003	OK	OK	OK	OK	outlier
17	Bruker 600, 2014	OK	OK	OK	outlier	outlier
18	Bruker 600, 2014	OK	OK	OK	OK	outlier
19	Bruker 600, 2009	OK	OK	OK	OK	OK
20	Bruker 400, 2010	OK	OK	OK	OK	outlier
21	Bruker 600, 1998	OK	OK	OK	OK	OK
22	Bruker 400, 2014	OK	OK	OK	OK	OK
23	Bruker 700, 2010	OK	OK	OK	OK	outlier
24	Bruker 500, 1987	OK	OK	OK	OK	OK
25	Bruker 400, 2003	OK	OK	OK	OK	outlier
26	Bruker 600, 2006	OK	OK	OK	outlier	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	OK	OK	OK	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	OK
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	OK	outlier
32	Bruker 500, 2001	OK	OK	OK	outlier	outlier
33	Bruker 400, 2000	OK	OK	OK	OK	outlier
34	Agilent 500, 2008	OK	OK	OK	OK	outlier
35	Bruker 400, 2009	OK	OK	OK	OK	OK
36	Bruker 600, 1991	OK	OK	OK	OK	OK
37	Bruker 500, 2014	OK	OK	OK	OK	outlier
38	Varian 400, 1997	OK	OK	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	outlier
40	Agilent 500, 2014	OK	OK	OK	outlier	outlier
41	Bruker 500, 2004	OK	OK	OK	OK	outlier
42	Bruker 700, 2001	outlier	outlier	outlier	outlier	outlier
43	Bruker 400, 2015	OK	OK	OK	OK	outlier
44	Jeol 600, 2016	OK	OK	OK	OK	outlier
45	Bruker 600, 2007	OK	OK	OK	OK	OK
46	Bruker 500, 2014	OK	OK	OK	OK	outlier
47	Bruker 500, 2014	OK	OK	OK	OK	outlier
48	Bruker 400, 2005	outlier	outlier	outlier	outlier	outlier
49	Bruker 500, 2017	OK	OK	OK	OK	OK
50	Bruker 400, 2016	OK	OK	outlier	outlier	outlier
51	Bruker 500, 2010	OK	outlier	outlier	outlier	outlier
52	Bruker 400, 2011	OK	OK	OK	OK	outlier
53	Agilent 500, 2015	OK	OK	OK	OK	OK
54	Bruker 400, 2016	OK	OK	OK	OK	OK
55	Bruker 500, 2004	OK	OK	OK	OK	OK
56	Bruker 700, 2013	OK	OK	OK	OK	outlier
57	Bruker 400, 2012	OK	OK	OK	OK	outlier
58	Varian 400, 2013	OK	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	OK	OK
60	Jeol 600, 2016	OK	OK	OK	OK	outlier
61	Bruker 300, 2001	OK	OK	outlier	outlier	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	outlier
63	Jeol 600, 2016	OK	OK	OK	OK	OK
64	Jeol 300, 2000	OK	OK	outlier	outlier	outlier
65	Bruker 400, 2012	OK	OK	OK	OK	OK
	n	63	60	56	51	18

Table S6. qNMR analysis of glucose (S6)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of glucose (S6 at 4.58 - 4.71 ppm).

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y* -intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	OK	OK	outlier
2	Varian 500, 2002	OK	OK	OK	OK	outlier
3	Varian 700, 2005	OK	OK	OK	OK	outlier
4	Bruker 600, 2006	OK	OK	OK	OK	outlier
5	Bruker 600, 2007	OK	OK	OK	outlier	outlier
6	Bruker 500, 2016	OK	outlier	outlier	outlier	outlier
7	Bruker 400, 2002	OK	OK	OK	OK	outlier
8	Bruker 500, 2014	OK	OK	OK	OK	outlier
9	Bruker 400, 2010	OK	OK	OK	OK	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	outlier
11	Bruker 400, 2013	OK	OK	OK	OK	outlier
12	Bruker 500, 2016	OK	OK	OK	OK	outlier
13	Bruker 600, 1999	OK	OK	OK	OK	outlier
14	Bruker 600, 2007	OK	OK	OK	OK	outlier
15	Bruker 600, 2014	OK	OK	OK	OK	outlier
16	Bruker 400, 2003	OK	OK	OK	OK	OK
17	Bruker 600, 2014	OK	OK	OK	OK	outlier
18	Bruker 600, 2014	OK	OK	OK	OK	outlier
19	Bruker 600, 2009	OK	OK	OK	OK	outlier
20	Bruker 400, 2010	OK	OK	OK	OK	outlier
21	Bruker 600, 1998	OK	OK	OK	OK	outlier
22	Bruker 400, 2014	OK	OK	OK	OK	outlier
23	Bruker 700, 2010	OK	OK	OK	OK	outlier
24	Bruker 500, 1987	OK	OK	OK	OK	OK
25	Bruker 400, 2003	OK	OK	OK	OK	outlier
26	Bruker 600, 2006	OK	OK	OK	OK	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	OK	OK	OK	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	outlier
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	OK	outlier
32	Bruker 500, 2001	OK	OK	OK	OK	OK
33	Bruker 400, 2000	OK	OK	OK	OK	outlier
34	Agilent 500, 2008	OK	OK	OK	OK	outlier
35	Bruker 400, 2009	OK	OK	OK	OK	outlier
36	Bruker 600, 1991	OK	OK	OK	OK	outlier
37	Bruker 500, 2014	OK	OK	OK	OK	outlier
38	Varian 400, 1997	OK	OK	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	OK
40	Agilent 500, 2014	OK	OK	OK	OK	outlier
41	Bruker 500, 2004	OK	outlier	outlier	outlier	outlier
42	Bruker 700, 2001	OK	outlier	outlier	outlier	outlier
43	Bruker 400, 2015	OK	OK	OK	OK	outlier
44	Jeol 600, 2016	OK	OK	OK	OK	outlier
45	Bruker 600, 2007	OK	OK	OK	OK	outlier
46	Bruker 500, 2014	OK	OK	OK	OK	OK
47	Bruker 500, 2014	OK	OK	OK	OK	OK
48	Bruker 400, 2005	OK	outlier	outlier	outlier	outlier
49	Bruker 500, 2017	OK	outlier	outlier	outlier	outlier
50	Bruker 400, 2016	OK	outlier	outlier	outlier	outlier
51	Bruker 500, 2010	OK	OK	OK	OK	outlier
52	Bruker 400, 2011	OK	outlier	outlier	outlier	outlier
53	Agilent 500, 2015	OK	OK	OK	outlier	outlier
54	Bruker 400, 2016	OK	OK	OK	OK	outlier
55	Bruker 500, 2004	OK	OK	OK	OK	outlier
56	Bruker 700, 2013	OK	OK	OK	OK	outlier
57	Bruker 400, 2012	OK	OK	OK	OK	outlier
58	Varian 400, 2013	outlier	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	OK	OK
60	Jeol 600, 2016	OK	OK	OK	OK	outlier
61	Bruker 300, 2001	OK	OK	OK	OK	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	outlier
63	Jeol 600, 2016	OK	OK	OK	OK	outlier
64	Jeol 300, 2000	OK	OK	OK	OK	OK
65	Bruker 400, 2012	OK	outlier	outlier	outlier	outlier
	n	64	55	54	52	9

Table S7. qNMR analysis of glucose (S7)

Selection process applied to the calibration curves produced by the ILC participants for the qNMR analysis of glucose (S7 at 5.15 - 5.31 ppm).

	Spectrometer	F test for linearity	Huber-Cochran tests on slopes	Huber-Cochran tests on *y*-intercepts	Parallelism test	Coincidence test
1	Bruker 400, 2006	OK	OK	OK	OK	outlier
2	Varian 500, 2002	OK	OK	OK	OK	outlier
3	Varian 700, 2005	OK	OK	OK	OK	outlier
4	Bruker 600, 2006	OK	OK	OK	OK	outlier
5	Bruker 600, 2007	OK	OK	OK	OK	outlier
6	Bruker 500, 2016	outlier	outlier	outlier	outlier	outlier
7	Bruker 400, 2002	OK	OK	OK	OK	outlier
8	Bruker 500, 2014	OK	OK	OK	OK	OK
9	Bruker 400, 2010	OK	OK	OK	OK	outlier
10	Bruker 600, 2010	OK	OK	OK	OK	outlier
11	Bruker 400, 2013	OK	OK	OK	OK	outlier
12	Bruker 500, 2016	OK	outlier	outlier	outlier	outlier
13	Bruker 600, 1999	OK	OK	OK	OK	outlier
14	Bruker 600, 2007	OK	OK	OK	OK	OK
15	Bruker 600, 2014	OK	OK	OK	OK	OK
16	Bruker 400, 2003	OK	OK	OK	outlier	outlier
17	Bruker 600, 2014	outlier	outlier	outlier	outlier	outlier
18	Bruker 600, 2014	OK	OK	OK	OK	OK
19	Bruker 600, 2009	OK	OK	OK	OK	outlier
20	Bruker 400, 2010	OK	OK	OK	OK	outlier
21	Bruker 600, 1998	OK	OK	OK	OK	OK
22	Bruker 400, 2014	OK	OK	OK	OK	outlier
23	Bruker 700, 2010	OK	OK	OK	outlier	outlier
24	Bruker 500, 1987	OK	OK	OK	outlier	outlier
25	Bruker 400, 2003	OK	OK	OK	OK	outlier
26	Bruker 600, 2006	OK	OK	OK	OK	outlier
27	Agilent 600, 2001	OK	outlier	outlier	outlier	outlier
28	Bruker 400, 2010	OK	OK	OK	outlier	outlier
29	Bruker 400, 2013	OK	OK	OK	OK	outlier
30	Bruker 500, 2000	OK	OK	OK	OK	OK
31	Bruker 700, 2006	OK	OK	OK	OK	outlier
32	Bruker 500, 2001	OK	OK	OK	OK	outlier
33	Bruker 400, 2000	outlier	outlier	outlier	outlier	outlier
34	Agilent 500, 2008	OK	OK	OK	OK	OK
35	Bruker 400, 2009	OK	OK	OK	OK	outlier
36	Bruker 600, 1991	OK	OK	OK	OK	outlier
37	Bruker 500, 2014	OK	OK	OK	OK	outlier
38	Varian 400, 1997	OK	OK	outlier	outlier	outlier
39	Agilent 500, 2014	OK	OK	OK	OK	outlier
40	Agilent 500, 2014	OK	OK	OK	OK	outlier
41	Bruker 500, 2004	OK	OK	OK	OK	outlier
42	Bruker 700, 2001	outlier	outlier	outlier	outlier	outlier
43	Bruker 400, 2015	OK	OK	OK	OK	outlier
44	Jeol 600, 2016	OK	OK	OK	OK	outlier
45	Bruker 600, 2007	OK	OK	OK	OK	outlier
46	Bruker 500, 2014	OK	OK	OK	OK	OK
47	Bruker 500, 2014	OK	OK	OK	OK	OK
48	Bruker 400, 2005	outlier	outlier	outlier	outlier	outlier
49	Bruker 500, 2017	OK	OK	OK	outlier	outlier
50	Bruker 400, 2016	OK	outlier	outlier	outlier	outlier
51	Bruker 500, 2010	OK	OK	OK	OK	outlier
52	Bruker 400, 2011	OK	OK	OK	OK	OK
53	Agilent 500, 2015	OK	OK	OK	OK	OK
54	Bruker 400, 2016	OK	OK	OK	OK	outlier
55	Bruker 500, 2004	OK	OK	OK	OK	outlier
56	Bruker 700, 2013	OK	OK	OK	OK	outlier
57	Bruker 400, 2012	OK	outlier	outlier	outlier	outlier
58	Varian 400, 2013	outlier	outlier	outlier	outlier	outlier
59	Bruker 400, 2015	OK	OK	OK	OK	outlier
60	Jeol 600, 2016	OK	OK	OK	OK	OK
61	Bruker 300, 2001	OK	OK	OK	outlier	outlier
62	Bruker 600, 2016	OK	OK	OK	OK	OK
63	Jeol 600, 2016	OK	OK	OK	OK	OK
64	Jeol 300, 2000	OK	OK	OK	OK	outlier
65	Bruker 400, 2012	OK	OK	OK	OK	outlier
	n	59	55	54	48	14

Table S8. Performance of the selected laboratories for the qNMR analysis of S1 – S7

For each repeatable predicted concentration (according to Huber-Cochran tests) is reported the corresponding z-score value (acceptable values in green, questionable values in orange). n.r. not repeatable predicted concentration according to Huber-Cochran tests. N, number of metabolite concentrations which resulted reproducible for each laboratory. N, number of predicted concentrations which resulted reproducible for each metabolite during the interlaboratory comparison. PRSD, predicted relative standard deviation according to the Horwitz equation. RSD, relative standard deviation for each metabolite calculated considering the predicted concentrations which resulted repeatable according to the Huber-Cochran tests. HorRat, Horwitz ratio as $RSD\%/PRSD\%$.

		Parallel curves								Coincident curves							
	Spectrometer	S1	S2	S3	S4	S5	S6	S7	n	S1	S2	S3	S4	S5	S6	S7	n
1	Bruker 400, 2006	n.r.	2.26	-0.82	2.17	1.63	-1.24	-0.50	6	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
2	Varian 500, 2002	-0.31	0.05	0.46	0.43	0.38	0.38	-0.20	7	-0.27	0.27	n.r	n.r	n.r	n.r	n.r	2
3	Varian 700, 2005	n.r.	-0.42	0.64	0.57	0.41	0.33	-0.48	6	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
4	Bruker 600, 2006	n.r.	-0.23	0.30	-0.75	-0.51	0.77	0.02	6	n.r	-0.46	n.r	n.r	n.r	n.r	n.r	1
5	Bruker 600, 2007	-0.36	n.r.	0.54	-0.42	0.84	n.r	-1.54	5	n.r	n.r	n.r	n.r	0.75	n.r	n.r	1
6	Bruker 500, 2016	n.r.	1.26	-0.61	0.62	-1.38	n.r	n.r	4	n.r	n.r	n.r	0.60	n.r	n.r	n.r	1
7	Bruker 400, 2002	n.r.	0.44	-0.80	1.83	1.37	-0.26	-0.40	6	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
8	Bruker 500, 2014	-0.16	-1.20	n.r.	1.77	1.51	0.13	-0.84	6	n.r	n.r	n.r	1.71	1.59	n.r	-0.18	2
9	Bruker 400, 2010	n.r.	-0.43	0.80	0.87	0.35	-0.88	0.46	6	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
10	Bruker 600, 2010	-1.29	-0.30	n.r.	-1.06	-0.44	1.91	1.69	6	-1.30	-0.65	n.r	n.r	n.r	n.r	n.r	2
11	Bruker 400, 2013	n.r.	2.42	0.81	n.r.	1.38	-0.94	1.70	5	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
12	Bruker 500, 2016	0.18	-0.46	-0.39	-0.58	-1.00	-0.35	n.r	6	0.26	n.r	-1.31	-0.58	n.r	n.r	n.r	3
13	Bruker 600, 1999	-2.04	n.r.	0.16	0.73	0.43	0.30	-0.26	6	-2.10	n.r	n.r	n.r	n.r	n.r	n.r	1
14	Bruker 600, 2007	0.23	0.50	1.12	-0.18	n.r.	0.87	-0.18	6	0.31	n.r	1.54	n.r	n.r	n.r	1.14	2
15	Bruker 600, 2014	0.95	0.27	-0.31	-0.64	-1.67	0.56	-0.61	7	1.08	n.r	-1.16	-0.63	n.r	n.r	n.r	3
16	Bruker 400, 2003	-1.19	-1.23	0.00	-0.11	1.27	-1.16	n.r	6	-1.19	n.r	n.r	-0.11	n.r	-1.11	n.r	3
17	Bruker 600, 2014	0.11	n.r.	-0.29	-1.38	n.r.	0.69	n.r	4	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
18	Bruker 600, 2014	n.r.	0.64	n.r.	n.r.	-1.96	2.04	2.06	4	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
19	Bruker 600, 2009	0.93	0.74	0.05	0.24	0.76	1.89	0.30	7	n.r	n.r	-0.48	n.r	0.65	n.r	n.r	2
20	Bruker 400, 2010	n.r.	n.r.	1.97	0.79	0.50	-0.64	0.97	5	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
21	Bruker 600, 1998	n.r.	-0.18	0.33	-0.86	-0.72	0.66	-0.32	6	n.r	-0.33	0.04	-0.85	-1.22	n.r	0.85	4
22	Bruker 400, 2014	0.86	0.55	1.30	0.60	0.41	-1.20	1.14	7	0.98	n.r	n.r	n.r	0.20	n.r	n.r	2
23	Bruker 700, 2010	n.r.	-0.69	n.r.	-0.47	-0.45	0.30	n.r	4	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
24	Bruker 500, 1987	0.89	0.89	0.17	1.18	1.08	-0.29	n.r	6	1.01	2.45	n.r	1.14	1.06	0.59	n.r	5
25	Bruker 400, 2003	n.r.	n.r.	0.13	-0.41	-0.75	-0.80	-0.53	5	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
26	Bruker 600, 2006	n.r.	1.22	n.r.	n.r.	n.r.	2.33	2.19	3	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
27	Agilent 600, 2001	n.r.	n.r.	n.r.	n.r.	n.r.	n.r	n.r	0	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
28	Bruker 400, 2010	n.r.	n.r.	n.r.	n.r.	n.r.	-0.51	n.r	1	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
29	Bruker 400, 2013	1.57	0.52	0.72	0.40	0.07	-0.95	0.47	7	1.73	n.r	n.r	n.r	-0.22	n.r	n.r	2
30	Bruker 500, 2000	0.34	-0.03	-0.19	0.14	-0.09	-0.37	-0.50	7	0.42	0.05	-0.95	0.12	-0.42	0.43	0.50	6
31	Bruker 700, 2006	-1.46	0.09	n.r.	-1.02	-0.99	0.27	-1.63	6	-1.49	n.r	n.r	n.r	n.r	n.r	n.r	1
32	Bruker 500, 2001	-0.19	-0.11	-1.26	0.72	n.r.	-0.89	-1.32	6	-0.13	-0.16	n.r	0.69	n.r	-0.59	n.r	4
33	Bruker 400, 2000	n.r.	-0.56	0.22	-0.14	0.38	-0.64	n.r	5	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
34	Agilent 500, 2008	2.82	n.r.	0.78	-0.19	-0.42	1.66	1.58	6	n.r	n.r	n.r	-0.19	n.r	n.r	n.r	1
35	Bruker 400, 2009	-0.49	n.r.	0.98	0.13	0.00	-0.77	0.49	6	-0.46		1.26	0.12	-0.31	n.r	n.r	4
36	Bruker 600, 1991	0.75	2.46	0.21	0.87	0.89	0.90	0.62	7	0.87	n.r	-0.19	0.84	0.81	n.r	n.r	4
37	Bruker 500, 2014	-1.11	-1.26	-0.66	n.r.	-0.51	0.58	0.95	6	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
38	Varian 400, 1997	n.r.	n.r.	n.r.	n.r.	n.r.	n.r	n.r	0	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
39	Agilent 500, 2014	0.57	-0.62	-1.31	0.83	0.61	-0.23	-0.94	7	0.67	-1.47	n.r	n.r	n.r	0.71	n.r	3
40	Agilent 500, 2014	n.r.	n.r.	-1.84	-1.05	n.r.	0.65	0.46	4	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
41	Bruker 500, 2004	0.29	0.11	-0.78	0.52	-0.02	n.r	-0.87	6	0.38	0.42	n.r	n.r	n.r	n.r	n.r	2
42	Bruker 700, 2001	n.r.	n.r.	n.r.	-1.43	n.r.	n.r	n.r	1	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
43	Bruker 400, 2015	n.r.	-0.40	0.76	0.60	0.33	-0.91	0.52	6	n.r	-0.92	n.r	n.r	n.r	n.r	n.r	1
44	Jeol 600, 2016	n.r.	n.r.	-0.04	0.84	-0.02	0.72	-0.11	5	n.r	n.r	n.r	0.81	n.r	n.r	n.r	1
45	Bruker 600, 2007	n.r.	-0.55	0.74	-1.23	-0.74	0.27	-0.48	6	n.r	-1.28	0.80	n.r	-1.24	n.r	n.r	3
46	Bruker 500, 2014	-0.45	-0.89	n.r.	-0.52	-0.46	-0.95	-1.51	6	n.r	n.r	n.r	n.r	n.r	-0.70	-1.53	1
47	Bruker 500, 2014	n.r.	-0.90	-1.55	-1.12	-1.14	-1.12	-1.35	6	n.r	n.r	n.r	n.r	n.r	-1.02	-1.20	1
48	Bruker 400, 2005	n.r.	n.r.	n.r.	-2.73	n.r.	n.r	n.r	1	n.r	n.r	n.r	-2.67	n.r	n.r	n.r	1
49	Bruker 500, 2017	0.05	-0.84	n.r.	1.61	n.r.	n.r	n.r	3	0.12	n.r	n.r	n.r	n.r	n.r	n.r	1
50	Bruker 400, 2016	-1.64	-1.57	-0.82	n.r.	n.r.	n.r	n.r	3	-1.67	n.r	n.r	n.r	n.r	n.r	n.r	1
51	Bruker 500, 2010	n.r.	2.05	-2.16	1.07	n.r.	-0.55	-0.66	5	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
52	Bruker 400, 2011	n.r.	n.r.	1.25	-1.54	2.54	n.r	2.09	4	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
53	Agilent 500, 2015	0.56	-0.15	-0.32	0.61	0.80	n.r	-0.59	6	0.66	-0.27	-1.18	0.58	0.70	n.r	0.32	5
54	Bruker 400, 2016	n.r.	-1.18	n.r.	-1.22	-2.14	-0.17	0.83	5	n.r	n.r	n.r	-1.20	n.r	n.r	n.r	1
55	Bruker 500, 2004	0.36	0.05	0.29	0.72	0.50	0.27	0.10	7	0.45	0.27	-0.04	0.69	0.33	n.r	n.r	5
56	Bruker 700, 2013	n.r.	n.r.	1.23	0.21	-0.22	1.01	-0.39	5	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
57	Bruker 400, 2012	n.r.	n.r.	-2.37	0.86	0.05	-2.20	n.r	4	n.r	n.r	n.r	0.83	n.r	n.r	n.r	1
58	Varian 400, 2013	n.r.	n.r.	n.r.	n.r.	n.r.	n.r	n.r	0	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
59	Bruker 400, 2015	0.70	0.35	n.r.	0.49	0.71	0.27	0.30	6	0.81	1.05	n.r	0.47	0.59	1.69	n.r	5
60	Jeol 600, 2016	-0.28	-0.56	-2.10	-0.99	-1.80	-0.11	-1.34	7	n.r	n.r	n.r	n.r	n.r	n.r	-1.18	0
61	Bruker 300, 2001	n.r.	-1.44	n.r.	n.r.	n.r.	-2.41	n.r	2	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
62	Bruker 600, 2016	-1.02	-1.03	0.98	-0.03	0.26	-0.15	-0.70	7	-1.01	n.r	1.26	-0.04	n.r	n.r	0.10	3
63	Jeol 600, 2016	-0.18	0.35	0.52	-1.04	-0.91	0.75	-0.15	7	-0.12	1.04	0.40	-1.02	-1.46	n.r	1.19	5
64	Jeol 300, 2000	n.r.	n.r.	-0.34	n.r.	n.r.	0.21	-0.55	3	n.r	n.r	n.r	n.r	n.r	n.r	n.r	0
65	Bruker 400, 2012	n.r.	n.r.	1.50	-1.33	-1.18	n.r	n.r	3	n.r	n.r	n.r	-1.31	-1.80	n.r	n.r	2
	N	32	45	48	54	49	52	47		24	15	13	22	16	8	10	
	PRSD%	10.01	7.04	3.15	3.16	3.12	3.19	3.16		10.01	7.04	3.15	3.16	3.12	3.19	3.16	
	RSD%	17.39	20.88	3.12	5.17	5.78	10.56	5.48		16.55	8.14	1.64	5.30	4.51	5.77	2.87	
	HorRat	1.74	2.97	0.99	1.64	1.85	3.31	1.73		1.65	1.16	0.52	1.68	1.44	1.81	0.91	