

Methylphosphonic acid as a ^{31}P -NMR standard for the quantitative determination of phosphorus in carbonated beverages

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Supplementary Material

Results of NMR measurements

Control of linearity

Na_2HPO_4 concentration compared to the area of Na_2HPO_4 peak

No. tube	Na_2HPO_4 concentration (mM)	Absolute area of peak			(Average absolute area \pm STDEV*) $\times 10^3$
		Tube a	Tube b	Tube c	
Exp1	2.4	68167.57	72975.51	66147.29	69 ± 4
Exp2	3.4	83477.68	100989.00	101755.25	95 ± 10
Exp3	4.5	114689.73	121459.03	118535.90	118 ± 3
Exp4	6.2	153290.50	158894.07	161089.75	158 ± 4

* - Standard deviation were calculated as follow:

$$STDEV = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}, \text{ where } N-1 \text{ is number of degrees of freedom.}$$

MPA concentration compared to the area of MPA peak.

No. tube	MPA concentration (mM)	Absolute area of peak ^a			(Average absolute area \pm STDEV) $\times 10^3$
		Tube a	Tube b	Tube c	
Exp1	2.5	65861.60	70669.05	63260.26	67 ± 4
Exp2	3.5	83578.59	93714.44	94217.83	91 ± 6
Exp3	4.6	123795.85	126596.85	126794.95	126 ± 2
Exp4	8.5	210967.93	205372.97	215921.98	211 ± 5

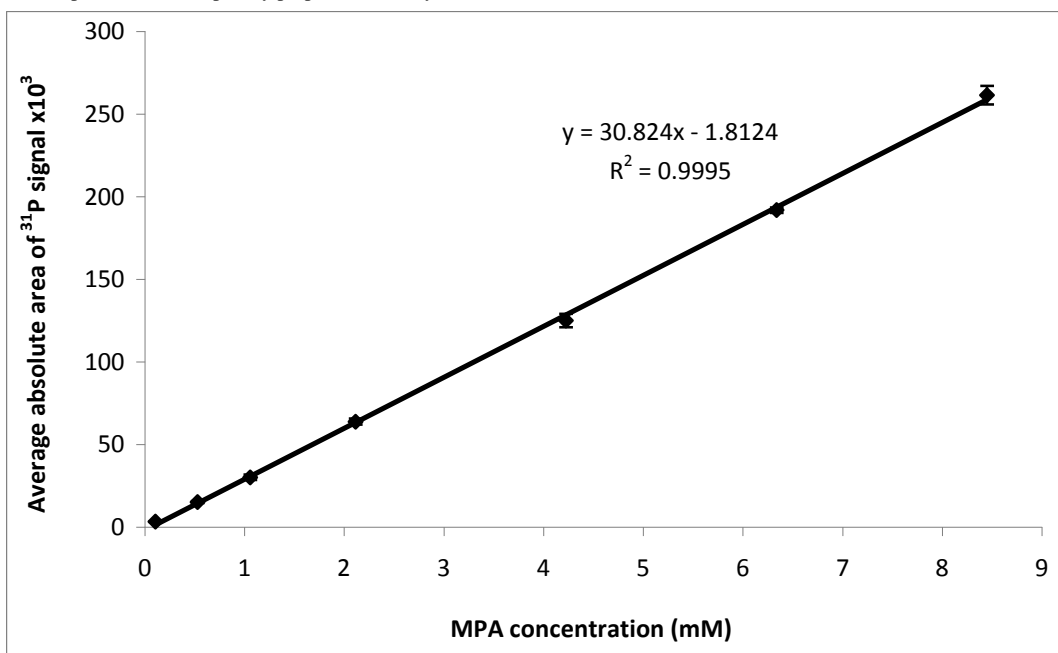
^a Three parallels were separately prepared for every concentration.

Control of linearity in soft drink (Coca-cola®)

MPA concentration compared to the area of MPA peak

No. tube	MPA concentration (mM)	Absolute area of peak ^a			(Average absolute area ± STDEV) × 10 ³
		Tube a	Tube b	Tube c	
Exp5	0.1	3205,204	3352,175	3084,813	3.2 ± 0.1
Exp6	0.5	14474,365	15739,012	15053,327	15.1 ± 0.6
Exp7	1.1	28174,86	30917,80	31126,67	30 ± 2
Exp8	2.1	61977,50	63773,71	65673,92	64 ± 2
Exp9	4.2	129294,75	121292,99	124421,51	125 ± 4
Exp10	6.3	191689,26	190250,07	193577,06	192 ± 2
Exp11	8.4	266910,70	261903,08	255699,96	262 ± 6

^a Three parallels were separately prepared for every concentration.



NMR measurements of carbonated beverages

<i>Cola 1</i> (with standard MPA concentration 7.0 mM in NMR tube)						
No. tube	30° pulse angle			90° pulse angle		
	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)
Exp1 ^a	1.86	1.00	5.68	1.96	1.00	5.39
Exp2	1.82	1.00	5.80	1.93	1.00	5.47
Exp3	1.86	1.00	5.68	1.92	1.00	5.50
Average (mM)			5.7	Average (mM)		5.5
STDEV (mM)			0.1	STDEV (mM)		0.1

^a Here and for following beverages three parallel samples were separately prepared (Exp 1, Exp 2, Exp 3).

<i>Cola 2</i> (with standard MPA concentration 7.0 mM in NMR tube)							
No. tube	30° pulse angle			90° pulse angle			
	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	
Exp1	1.78	1.00	5.93	1.88	1.00	5.62	
Exp2	1.65	1.00	6.40	1.75	1.00	6.04	
Exp3	1.81	1.00	5.84	1.91	1.00	5.53	
Average (mM)			6.1	Average (mM)			5.7
STDEV (mM)			0.3	STDEV (mM)			0.3

<i>Coca-Cola Zero</i> (with standard MPA concentration 7.0 mM in NMR tube)							
No. tube	30° pulse angle			90° pulse angle			
	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	
Exp1	2.23	1.00	4.74	2.31	1.00	4.57	
Exp2	2.24	1.00	4.72	2.40	1.00	4.40	
Exp3	2.28	1.00	4.63	2.39	1.00	4.42	
Average (mM)			4.7	Average (mM)			4.5
STDEV (mM)			0.1	STDEV (mM)			0.1

<i>Pepsi 1</i> (with standard MPA concentration 7.0 mM in NMR tube)							
No. tube	30° pulse angle			90° pulse angle			
	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	
Exp1	1.86	1.00	5.68	1.77	1.00	5.97	
Exp2	1.99	1.00	5.31	2.00	1.00	5.28	
Exp3	2.05	1.00	5.15	2.08	1.00	5.08	
Average (mM)			5.4	Average (mM)			5.4
STDEV (mM)			0.3	STDEV (mM)			0.5

<i>Dr. Pepper</i> (with standard MPA concentration 7.0 mM in NMR tube)							
No. tube	30° pulse angle			90° pulse angle			
	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)	
Exp1	2.97	1.00	3.56	2.96	1.00	3.57	
Exp2	3.04	1.00	3.47	3.09	1.00	3.42	
Exp3	2.94	1.00	3.59	3.06	1.00	3.45	
Average (mM)			3.5	Average (mM)			3.5
STDEV (mM)			0.1	STDEV (mM)			0.1

<i>Coca-Cola</i> (with standard MPA concentration 7.1 mM in NMR tube)			
No. tube	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)
Exp1	1.80	1.00	5.91
Exp2	1.69	1.00	6.30
Exp3	1.90	1.00	5.60
Average (mM)			5.9
STDEV (mM)			0.3

<i>Coca-Cola Light</i> (with standard MPA concentration 7.1 mM in NMR tube)			
No. tube	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)
Exp1	2.30	1.00	4.63
Exp2	2.32	1.00	4.59
Exp3	2.11	1.00	5.05
Average (mM)			4.8
STDEV (mM)			0.3

<i>Pepsi 2</i> (with standard MPA concentration 7.1 mM in NMR tube)			
No. tube	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)
Exp1	1.83	1.00	5.82
Exp2	1.77	1.00	6.01
Exp3	1.65	1.00	6.45
Average (mM)			6.1
STDEV (mM)			0.3

<i>Angry Birds Tropic Cola</i> (with standard MPA concentration 7.1 mM in NMR tube)			
No. tube	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)
Exp1	2.36	1.00	4.51
Exp2	2.02	1.00	5.27
Exp3	2.00	1.00	5.32
Average (mM)			5.0
STDEV (mM)			0.5

<i>RC Cola</i> (with standard MPA concentration 7.1 mM in NMR tube)			
No. tube	Normalized area of standard	Normalized area of phosphate	Concentration of phosphate (mM)
Exp1. #1 ^a	2.38	1.00	4.47
Exp1. #2	2.48	1.00	4.29
Exp1. #3	2.39	1.00	4.45
Exp2	2.39	1.00	4.45
Exp3	2.35	1.00	4.53
Average (mM)			4.4

STDEV (mM) 0.1

^a Sample 1 was measured 3 times.

Absolute area of ³¹P-NMR signal of 0.70 mM MPA in different cola matrixes measured with 30° and 90° pulse angle.

Beverage	30° pulse angle			90° pulse angle		
			(Average ± STDEV) × 10 ⁴			(Average ± STDEV) × 10 ⁴
Cola 1®	Exp1	91907,38	9.5 ± 0.3	Exp1	202754,38	21.2 ± 0.8
	Exp2	95956,23		Exp2	217199,16	
	Exp3	98624,55		Exp3	214725,02	
Cola 2®	Exp1	96832,08	9.3 ± 0.4	Exp1	217810,74	20.8 ± 0.9
	Exp2	91597,81		Exp2	200467,04	
	Exp3	89899,00		Exp3	205669,34	
Coca-Cola Zero®	Exp1	89984,13	8.9 ± 0.3	Exp1	193595,17	19.8 ± 0.7
	Exp2	85937,87		Exp2	193361,88	
	Exp3	91565,30		Exp3	206289,31	
Pepsi®	Exp1	85909,49	9.3 ± 0.7	Exp1	188497,84	21 ± 2
	Exp2	99046,92		Exp2	219779,94	
	Exp3	94881,34		Exp3	209720,66	
Dr.Pepper®	Exp1	95004,14	9.7 ± 0.4	Exp1	208196,93	21.0 ± 0.5
	Exp2	102162,09		Exp2	214822,85	
	Exp3	95279,84		Exp3	206039,50	

Results of spectrometric analysis^a.

Beverage	Concentration of phosphate, mgP/l (three parallels)		
Cola 1®	171	173	173
Cola 2®	171	174	172
Coca-Cola Zero®	150	148	148
Pepsi®	169	173	173
Dr.Pepper®	116	114	112

^a Determined by EVS-EN ISO 6878, sec 4 in accredited Central Lab of Estonian Environmental Research Centre