Supporting Information

Quantitative NMR of quadrupolar nucleus as a novel analytical method : Hydrolysis behavior analysis of aluminum ion

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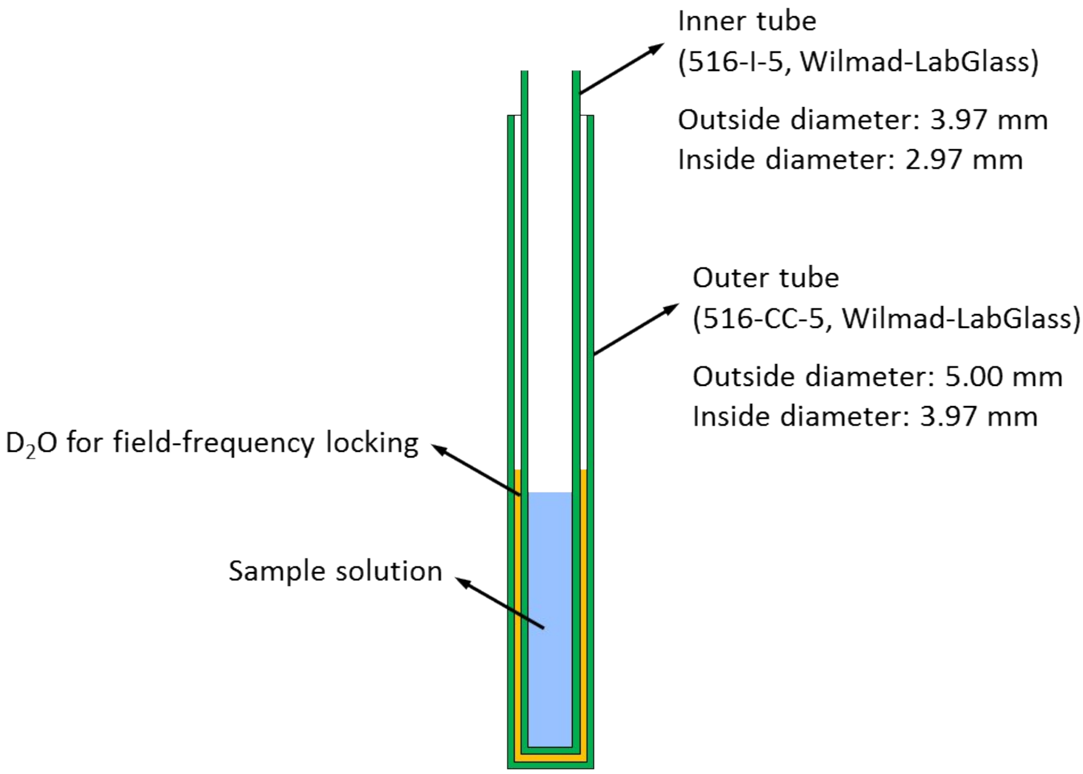
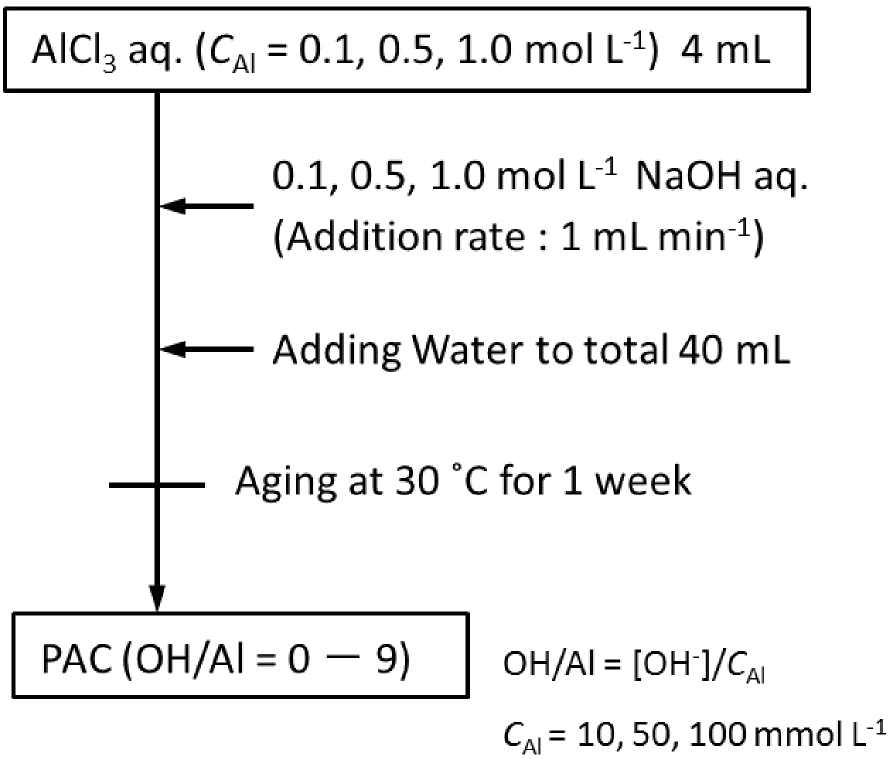
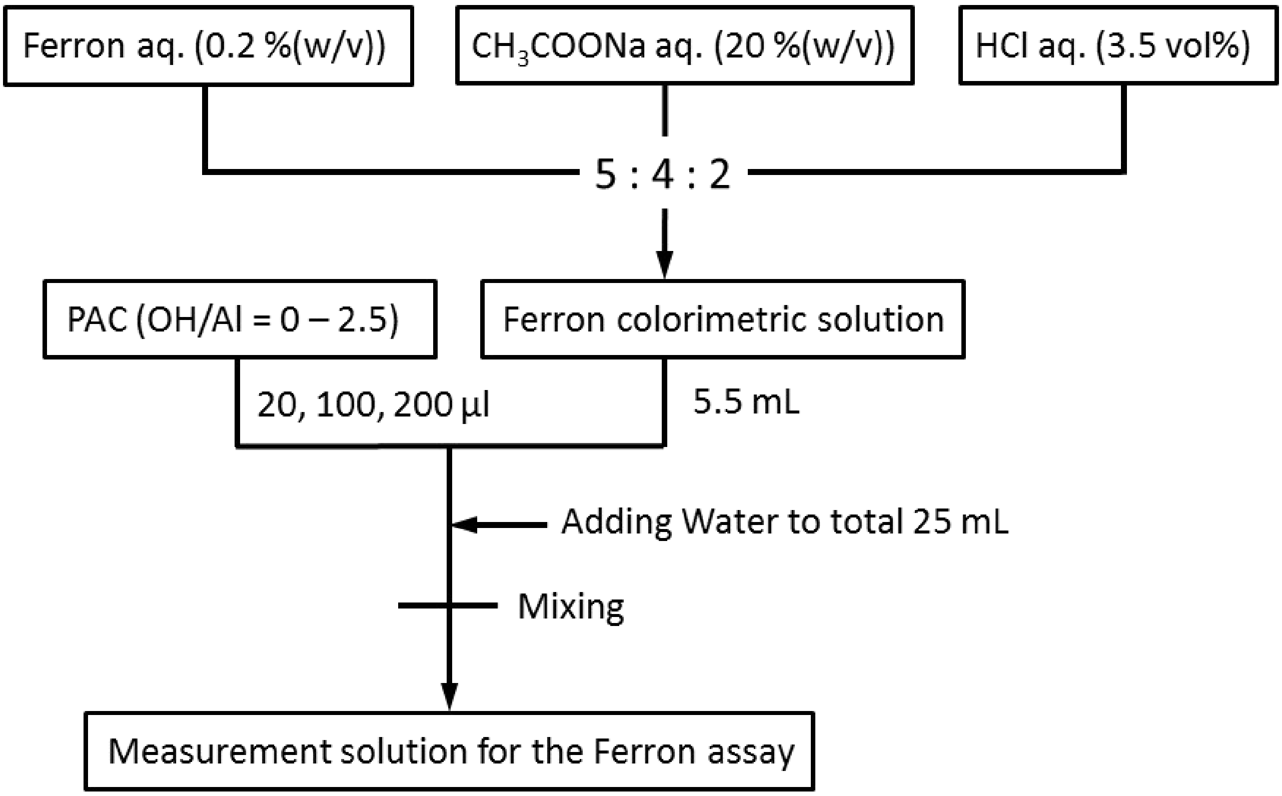


Scheme S1. Coaxial NMR tube system to avoid the contamination of D_2O for field-frequency locking into the sample solutions.



Scheme S2. Preparation of PAC sample solutions.



Scheme S3. Preparation of measurement solution for the Ferron assay.

Table S1. All raw data for the relationships between the integrated intensities per FID scan (I_{freeAl}) of ^{27}Al NMR signals due to $[Al(H_2O)_6]^{3+}$ ion in x molL^{-1} $Al(NO_3)_3$ + 0.1 molL^{-1} HNO_3 aq. (x = ca. 0.1 – 1 mol L^{-1}) at 30 °C and the $[Al(H_2O)_6]^{3+}$ concentrations (C_{freeAl}) as shown in Figs. 1(a) and 1(b). The I_{freeAl} values are converted into the values before the input into the RF amplifier in an NMR spectrometer (i.e., corresponding to the receiver gain of 0 dB).

C_{freeAl} (mmolL^{-1})	log (C_{freeAl}) (mmolL^{-1})	I_{freeAl}	log (I_{freeAl})
0.1173	-0.931	1.512×10^2	2.18
0.212	-0.673	4.49×10^2	2.65
0.446	-0.351	8.16×10^2	2.91
0.594	-0.226	1.015×10^3	3.01
0.959	-0.01800	1.571×10^3	3.20
2.19	0.340	3.60×10^3	3.56
3.51	0.546	6.17×10^3	3.79
5.55	0.744	9.53×10^3	3.98
7.20	0.858	1.236×10^4	4.09
8.85	0.947	1.475×10^4	4.17
20.0	1.301	3.01×10^4	4.48
40.0	1.602	6.38×10^4	4.80
60.0	1.778	8.99×10^4	4.95
80.0	1.903	1.232×10^5	5.09
100.0	2.00	1.656×10^5	5.22
197.7	2.30	3.26×10^5	5.51
368	2.57	6.05×10^5	5.78
568	2.75	9.30×10^5	5.97
752	2.88	1.265×10^6	6.10
935	2.97	1.602×10^6	6.20

Table S2. All raw data for the NMR measurement parameter dependences of the integrated intensities of ^{27}Al NMR signal (I_{freeAl}) due to $[Al(H_2O)_6]^{3+}$ ion ion in 0.1 mol L^{-1} $Al(NO_3)_3$ + 0.1 mol L^{-1} HNO_3 aq. at 30 °C as shown in Figs. 2(a) and 2(b). The I_{freeAl} values for Fig. 2(a) are converted into the values before the input into the RF amplifier in an NMR spectrometer (i.e., corresponding to the receiver gain of 0 dB). The integrated intensities for Fig. 2(b) are the values per FID scan.

(a) Number of FID scans dependence

Number of FID scans	I_{freeAl}
8	1.335×10^6
32	5.31×10^6
128	2.13×10^7
512	8.54×10^7
2048	3.41×10^8
8192	1.361×10^9

(b) Receiver gain dependence

Receiver gain (dB)	I_{freeAl}
6	3.42×10^5
10	5.46×10^5
16	1.084×10^6
20	1.763×10^6
26	3.35×10^6
30	5.32×10^6
36	1.111×10^7
40	1.671×10^7
46	3.41×10^7
50	5.48×10^7
56	1.041×10^8
60	1.660×10^8

Table S3. All raw data for the effect of the sample solution temperature on the relationships between the integrated intensities per FID scan of ^{27}Al NMR signals due to $[Al(H_2O)_6]^{3+}$ ion in x mol L^{-1} $Al(NO_3)_3$ + 0.1 mol L^{-1} HNO_3 aq. (x = ca. 1 – 1000 mmol L^{-1}) and the $[Al(H_2O)_6]^{3+}$ ion concentrations as shown in Figs. 3(a), 3(b), and 3(c). The I_{freeAl} values are converted into the values before the input into the RF amplifier in an NMR spectrometer (i.e., corresponding to the receiver gain of 0 dB).

(a) 21.4 °C (i.e., room temperature)

C_{reeAl} (mmol L^{-1})	log (C_{reeAl}) (mmol L^{-1})	I_{freeAl}	log (I_{freeAl})
1.020	0.00860	1.675×10^3	3.224
2.55	0.4065	4.26×10^3	3.629
5.10	0.7076	8.56×10^3	3.932
8.16	0.9117	1.340×10^4	4.127
10.20	1.0086	1.752×10^4	4.244
25.5	1.4065	4.36×10^4	4.640
51.0	1.7076	8.73×10^4	4.941
81.6	1.912	1.376×10^5	5.139
102.0	2.009	1.847×10^5	5.267
204	2.310	3.42×10^5	5.534
408	2.611	6.95×10^5	5.842
612	2.787	1.023×10^6	6.010
816	2.912	1.409×10^6	6.149
1020	3.009	1.829×10^6	6.262

(b) 30 °C

C_{reeAl} (mmol L^{-1})	log (C_{reeAl}) (mmol L^{-1})	I_{freeAl}	log (I_{freeAl})
1.020	0.00860	1.751×10^3	3.243
2.55	0.4065	4.00×10^3	3.602
5.10	0.7076	8.51×10^3	3.930
8.16	0.9117	1.337×10^4	4.126
10.20	1.0086	1.697×10^4	4.230
25.5	1.4065	4.29×10^4	4.632
51.0	1.7076	8.28×10^4	4.918
81.6	1.912	1.350×10^5	5.130
102.0	2.009	1.819×10^5	5.260
204	2.310	3.30×10^5	5.518
408	2.611	6.84×10^5	5.835
612	2.787	1.008×10^6	6.004
816	2.912	1.397×10^6	6.145
1020	3.009	1.718×10^6	6.235

(c) 40 °C

C_{reeAl} (mmol L^{-1})	log (C_{reeAl}) (mmol L^{-1})	I_{freeAl}	log (I_{freeAl})
1.020	0.00860	1.728×10^3	3.237
2.55	0.4065	4.05×10^3	3.608
5.10	0.7076	8.01×10^3	3.903
8.16	0.9117	1.244×10^4	4.095
10.20	1.0086	1.587×10^4	4.201
25.5	1.4065	4.03×10^4	4.606
51.0	1.7076	7.93×10^4	4.899
81.6	1.912	1.277×10^5	5.106
102.0	2.009	1.676×10^5	5.224
204	2.310	3.15×10^5	5.498
408	2.611	6.31×10^5	5.800
612	2.787	9.61×10^5	5.983
816	2.912	1.319×10^6	6.120
1020	3.009	1.649×10^6	6.217

Table S4. ^{27}Al spin-lattice and spin-spin relaxation times, i.e., T_1 and T_2, of all aluminum species were determined by the inversion recovery[40,41] and the CPMG procedure[42-44]. Total concentration of aluminum (C_{Al}) is 100 mmol L^{-1}.

Chemical shift	0 ppm	4.0 ppm	62.5 ppm	80 ppm
Species	$[Al(H_2O)_6]^{3+}$	Al_3	K-Al_{13}	$Al(OH)_4^-$
T_1 (s)	0.035*	0.0014*	0.040*	0.013**
T_2 (s)	0.028*	0.0015*	0.034*	0.011**

*Determined from the sample solution of OH/Al = 1.25

** Determined from the sample solution of OH/Al = 4.0

Table S5. Fitting parameters and reaction rate constant, *k*, which were derived from a nonlinear least squares curve fitting method by the Ferron assay of PAC aqueous solutions after aging for 1 week at 30 °C.

(a) C_{Al} = 10 mmol L^{-1}

OH/Al	A_0	A_∞	A_1	$A_2 (A_\infty - A_0)$	k_{b1}	k_{b2}	R
0	0.6195	0.6195	0.10407	0.08706	0.06992	0.0003217	0.94493
0.25	0.6038	0.6038	0.12627	0.14479	0.08261	0.0006955	0.98416
0.50	0.4211	0.6049	0.09437	0.18386	0.06458	0.0007862	0.99732
0.75	0.3575	0.6035	0.09765	0.2460	0.06689	0.0007310	0.99855
1.00	0.3369	0.6060	0.05104	0.2691	0.03981	0.0008570	0.99915
1.25	0.2672	0.5941	0.06389	0.3269	0.004192	0.0006971	0.99846
1.50	0.2174	0.5913	0.02435	0.3740	0.02190	0.0009467	0.99955
1.75	0.16400	0.5888	0.015752	0.4248	0.015287	0.0007925	0.99987
2.00	0.08985	0.5530	0.008229	0.4632	0.005048	0.0008749	0.99972
2.25	0.05528	0.5120	0.010663	0.4567	0.005728	0.0008047	0.99982
2.50	0.02796	0.2437	0.007243	0.2158	0.003333	0.0007019	0.99968

(b) C_{Al} = 50 mmol L^{-1}

OH/Al	A_0	A_∞	A_1	$A_2 (A_\infty - A_0)$	k_{b1}	k_{b2}	R
0	0.5307	0.6362	0.14077	0.10554	0.08851	0.0003644	0.88508
0.25	0.4467	0.6248	0.19666	0.17808	0.11930	0.0006671	0.95170
0.50	0.4375	0.6215	0.11327	0.18405	0.07564	0.0007569	0.99327
0.75	0.3926	0.6010	0.06683	0.2084	0.05035	0.0008850	0.99754
1.00	0.3853	0.6089	0.017868	0.2235	0.007634	0.0008993	0.99874
1.25	0.2785	0.5983	0.05081	0.3198	0.03886	0.0009583	0.99879
1.50	0.2358	0.5878	0.018443	0.3520	0.016507	0.0009977	0.99950
1.75	0.17947	0.5915	0.014217	0.4121	0.011904	0.0010337	0.99952
2.00	0.11594	0.5759	0.012572	0.4600	0.007566	0.0010691	0.99958
2.25	0.05709	0.5842	0.0144	0.5271	0.004990	0.0010608	0.99996
2.50	0.02796	0.2437	0.007243	0.2158	0.003333	0.0007019	0.99968

(c) C_{Al} = 100 mmol L^{-1}

OH/Al	A_0	A_∞	A_1	$A_2 (A_\infty - A_0)$	k_{b1}	k_{b2}	R
0	0.5527	0.6409	0.10405	0.08824	0.07064	0.0004093	0.95192
0.25	0.5535	0.6284	0.06248	0.07483	0.04912	0.0004495	0.99029
0.50	0.4999	0.6307	0.06622	0.13078	0.04930	0.0007246	0.99605
0.75	0.4226	0.6104	0.06912	0.18782	0.05072	0.0008799	0.99638
1.00	0.3808	0.6170	0.05163	0.2362	0.03986	0.0009378	0.99704
1.25	0.3036	0.6182	0.06082	0.3147	0.04484	0.00092114	0.99846
1.50	0.2615	0.6212	0.02837	0.3598	0.02505	0.00099744	0.99924
1.75	0.19763	0.5985	0.016816	0.4009	0.014226	0.0010621	0.99935
2.00	0.13216	0.6018	0.019884	0.4696	0.013553	0.0010489	0.99925
2.25	0.07495	0.5951	0.01534	0.5202	0.006760	0.0010835	0.99951
2.50	0.06341	0.3969	0.03926	0.3335	0.02276	0.0008521	0.99620

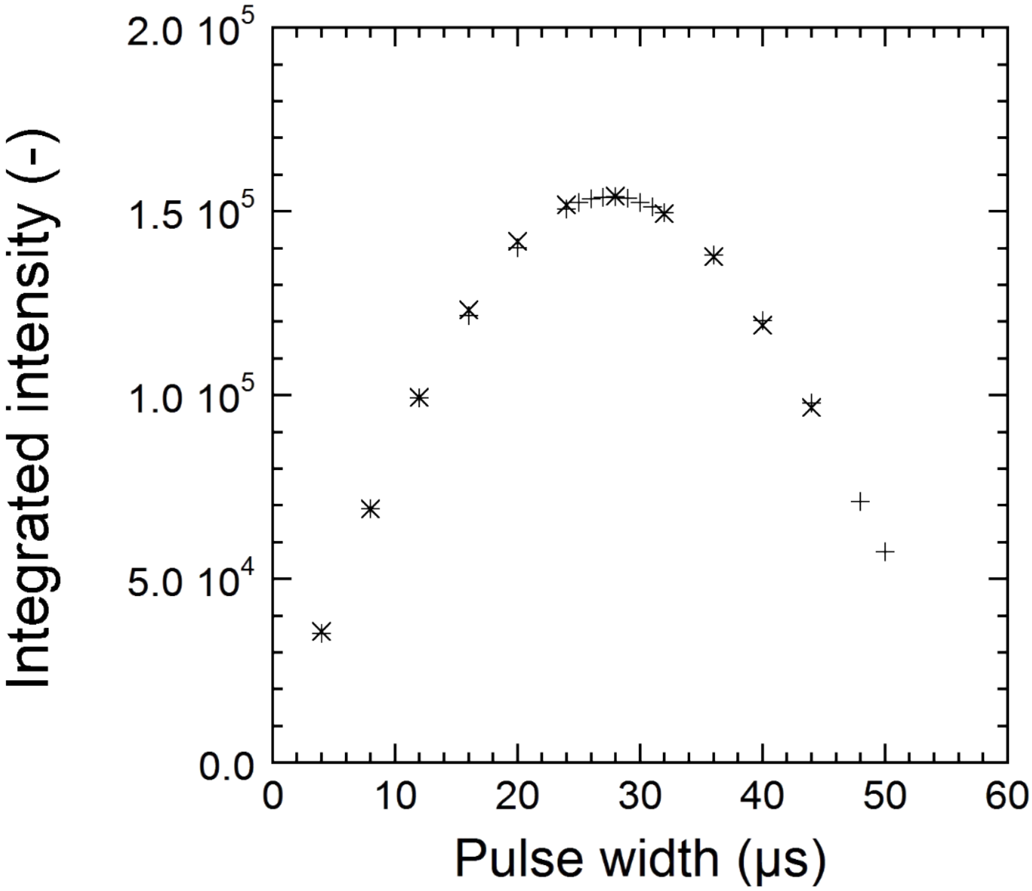
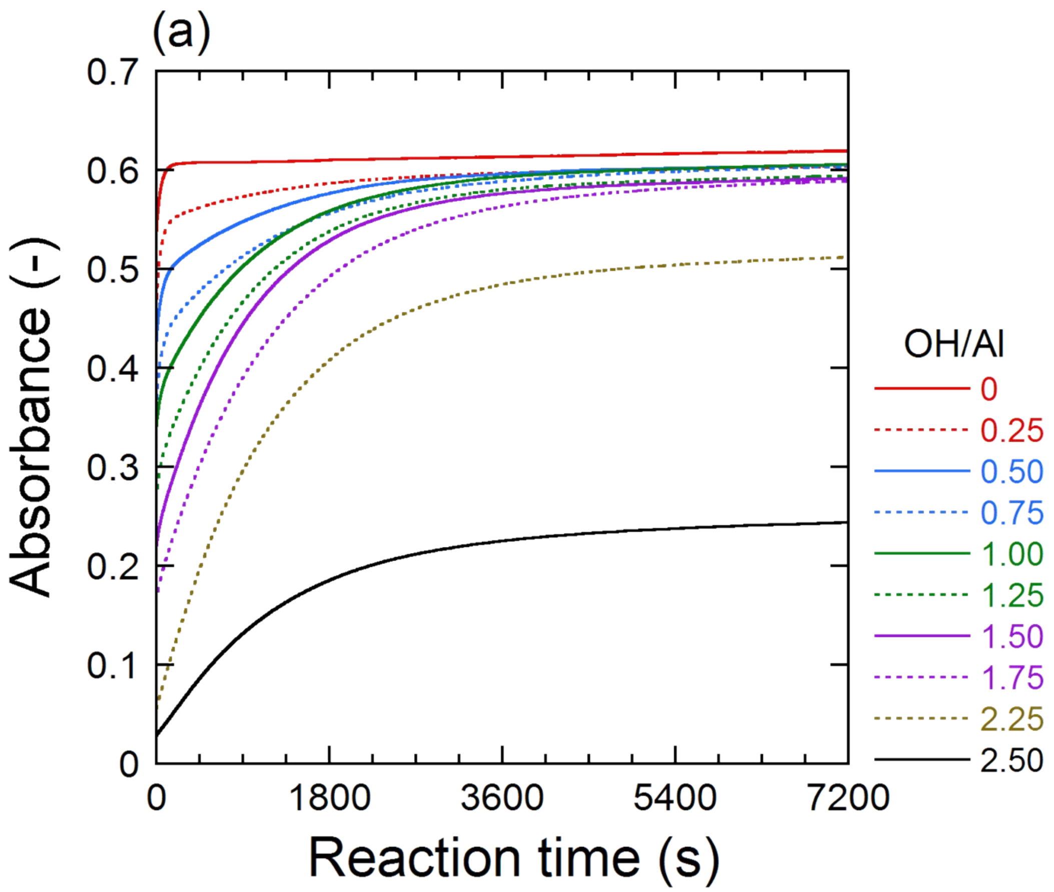


Fig. S1. Influence of anionic species on the pulse width dependence of the integrated intensities per FID scan (I_{freeAl}) of ^{27}Al NMR signals due to $[Al(H_2O)_6]^{3+}$ ion at 30 °C. The I_{freeAl} values are converted into the values before the input into the RF amplifier in an NMR spectrometer (i.e., corresponding to the receiver gain of 0 dB). Sample solution: (+) 0.1 mol L^{-1} $Al(NO_3)_3$ + 0.1 mol L^{-1} HNO_3, (×) 0.1 mol L^{-1} $AlCl_3$ + 0.1 mol L^{-1} HCl.


(a)
Absorbance (-)
Reaction time (s)
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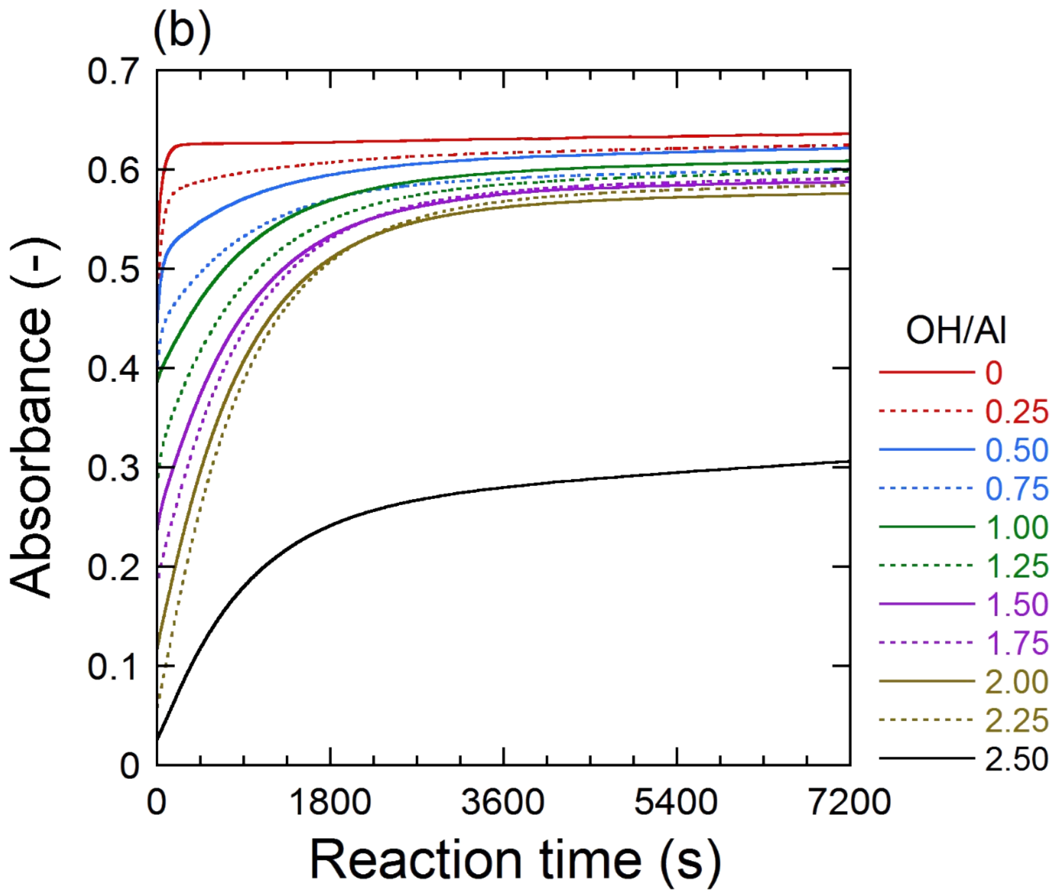
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1800
3600
5400
7200
OH/Al
0
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.25
2.50


(b)
Absorbance (-)
Reaction time (s)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1800
3600
5400
7200
OH/Al
0
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50

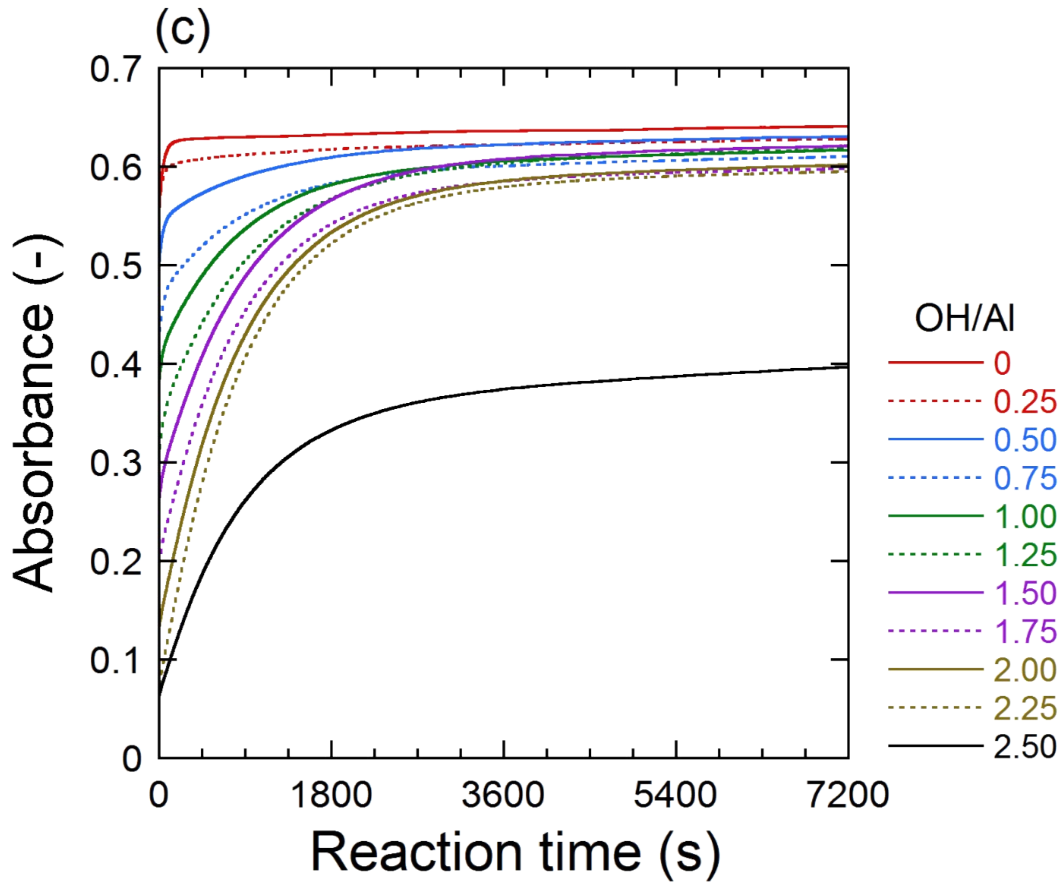


Fig. S2. Time course of absorbance for the Ferron assay of PAC aqueous solutions after aging for 1 week at 30 °C. Total concentration of aluminum: (a) 10 mmol L^{-1}, (b) 50 mmol L^{-1}, (c) 100 mmol L^{-1}.