

Effects of Cations and pH on Optimized Assessment of Prostatic Citrate at 3 Tesla

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INTRODUCTION It was previously demonstrated that existence of various cations and pH differences could affect chemical shifts, and the J-coupling of citrate protons (1). This implies that cation concentration and composition, and pH play important roles in echo time dependence of citrate signals. However, such effects have not been fully examined. Here, effects of cations and pH were investigated in optimization of TE for citrate assessment at 3T.

METHODS Citrate spectra from water solutions (2) shown in Table 1 were observed with a 3-T scanner (Signa VH/i, 8.3m4, GE Medical Systems), using Point RESolved Spectroscopy (PRESS) and the following conditions: TR, 1500 ms; spectral band width, 19.54 ppm (2500 Hz); voxel size, 20 × 20 × 10 mm; number of time data points, 2048; and number of acquisitions, 4. Echo time (TE) was set at 25 ms, 145 ms, and 30 ms to 320 ms in 10-ms steps. No water or lipid suppression was needed for the solution studies. Five healthy male volunteers (22 to 33 years old) were also examined using a quadrature transceive pelvic coil (3) with chemical shift selective water suppression and spectral spatial excitation pulses. Integrated areas of the observed citrate spectra were calculated with manufacturer supplied software (SAGE, GE Medical Systems) following standard signal processing accompanied with eddy current compensation by deduction of non-suppressed water signal phase. To further analyze experimental results, the density matrix formalism (4), was used to model the TE dependence of citrate signals. The J-coupling constant, J [Hz]; chemical shift difference between "A" and "B" protons, δ [Hz]; amplitude, A; signal decay rate, r_2 [1/s] = $1/T_2$; off-resonance frequency of citrate from the RF center, f_0 [Hz] were estimated from the density matrix modeling of the data.

RESULTS Effects of monovalent cations were not significant at low concentrations, but resulted in significant intensity changes at 145 mM sodium and 80 mM potassium. As an example for the divalent results, TE dependency of the citrate signal intensity in solutions with calcium chloride is shown in Fig. 1. Results obtained with pH 7.0 and 8.0 were not significantly different. TE dependency curve at pH 6.0 was higher than those at pH 7.0 and 8.0 at TE values shorter or equal to 120 ms, and lower at TE values longer than 240 ms, while that at pH 9.0 was generally lower across the TE values of 40 to 240 ms. Those intensity curve variations observed in individual cation solutions were not as prevalent within the three prostate mimicking phantoms (#18-20). On the other hand, the amplitudes of the curves at TE values larger than 25 ms for the volunteers significantly differed with each other, although the peak positions consistently appeared at 130 through 140 and around 250 ms. To analyze TE dependency changes in details, the density matrix model was fitted to the experimental data as shown in Fig. 2. The estimated J-coupling constant and T_2 of the citrate signal are shown in Table 2.

DISCUSSIONS Effects of divalent cations appeared as shifts or "shrinkages" of the curves in the TE direction. In spite of individual variations among the volunteers, whose J and T_2 values were evaluated as shown in Table 2, the peak at TE between 130 and 140 ms was consistently higher than that around 250 ms, because of T_2 decay. The shortest TE, i.e., 25 ms in the present study, also yielded consistently high intensity, but spectral contamination due to lipid signals at this TE might be problematic for spectroscopic imaging studies. Therefore, the optimized TE range for practical citrate observations at 3T is 130-140 ms. This optimum TE range at 3T lies in the same TE range as at 1.5T, despite differences in J modulation.

Solution	Sodium-Citrate	Citrate	NaCl	KCl	CaCl ₂	MgCl ₂	ZnCl ₂	pH ^a	pH adjustment ^b
1	90	0						8.59	No
2	90	0	20					8.59	No
3	90	0	40					8.59	No
4	90	0			10			8.58	No
5	90	0			20			8.55	No
6	90	0				10		8.58	No
7	90	0				20		8.51	No
8	90	0					10	7.67	No
9	90	0					20	7.27	No
10	total 90							6.01	Yes
11	total 90							7.01	Yes
12	total 90							7.99	Yes
13	total 90							9.00	Yes
14	total 45		143.7	37.6	10.4	8.4	4.5	7.55	Yes
15	total 90		145.0	61.0	18.0	14.7	8.5	7.10	Yes
16	total 135		146.4	84.4	25.7	21.0	12.6	6.65	Yes

^apH measurement was performed at 27.5-28.6 °C. ^bSince pH was adjusted by adding NaOH or HCl, actual Na⁺ and Cl⁻ concentrations were slightly higher than those listed in the table.

Table 2. Parameter estimations for the volunteers

Volunteers	J [Hz]	Citrate Proton T_2 [ms]
1	16.6	87.2
2	17.2	264
3	16.5	197
4	17.9	26.3
5	16.5	147

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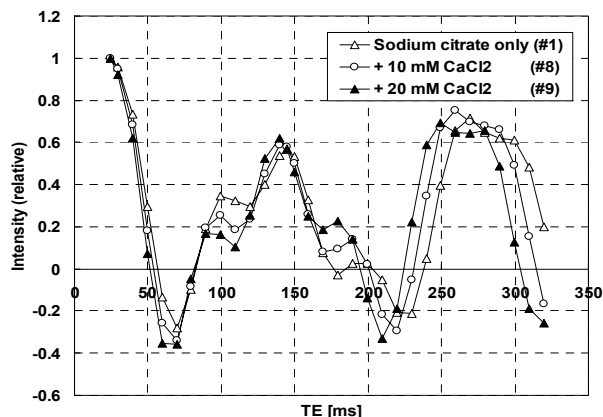


Fig. 1 Relationships between TE and citrate signal intensity in sodium citrate solutions with and without calcium chloride (#1, 4, and 5 in Table 1). Intensity was normalized against that obtained at TE = 25ms.

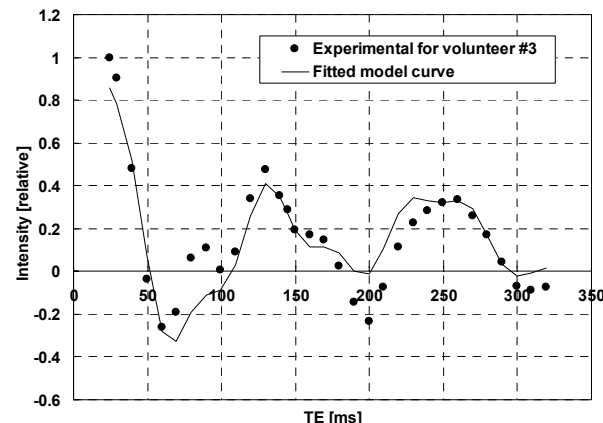


Fig. 2 Relationships between TE and citrate signal intensity for volunteer #2 fitted with the density matrix model function.