Investigation of the NMR dose response of a ceric sulfate dosimeter

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Introduction
Since 1984, the NMR ferrous sulfate chemical dosimeter has been used. The potential use of other paramagnetic substances, although suggested, have not previously been investigated. The ceric sulfate dosimeter has previously been used for high dose dosimetry using spectrophotometry but not NMR. Unlike the ferrous sulfate dosimeter, the ceric sulfate dosimeter relies on reduction rather than oxidation, the radiation-induced change of concentration of ceric (Ce⁴⁺) to cerous (Ce³⁺) being the measurable quantity. As paramagnetic cerous ions possess unpaired electrons and ceric ions do not, there is potential for using NMR to quantify absorbed radiation doses for this dosimeter. The purpose of this study was to examine the basic relationship between the NMR relaxation rates and absorbed radiation dose for the ceric sulfate dosimeter and its potential use as a gel dosimeter.

Materials and methods
Standard solutions of 20 mM Ce⁴⁺ (ammonium ceric sulfate) and 400 mM H₂SO₄ were prepared and transferred to 10 ml vials. Before use, the vials were thoroughly cleaned and heated. In between experiments the vials were filled with a standard solution which was exchanged with fresh solution before irradiation. Additionally, gel samples were also prepared with a composition of 1% agarose, 50 mM of H₂SO₄ and 20 mM ammonium ceric sulfate. All chemicals were of analytical grade and ultra purified water was used.

Irradiations were undertaken using a previously calibrated 60Co unit (220 Gammacell, MDS Nordion, Canada) with an absorbed dose rate of 0.107 kGy/minute.

Relaxation times were evaluated using a Siemens Vision 1.5 T MRI scanner. To obtain the T₁ data, a single spin echo sequence, echo time (TE) 12 ms and 21 repetition times (TR) ranging from 25 to 3800 ms were used. To obtain the T₂ data a customised 32 multi-spin-echo sequence with a TE of 50 ms and TR of 4000 ms.

Results and discussion
R₁ (1/T₁) (Figure 1) and R₂ (1/T₂) (Figure 2) dose responses were found to be approximately linear to 30 kGy with a similar slope of 0.0064±0.0004 and 0.0068±0.0009 s⁻¹kGy⁻¹, respectively. The correlation coefficients in this interval were significantly better for the R₁ than for R₂ measurements, r=0.995 compared with r=0.982. This may be due to sub-optimisation of TE and TR.

The gel samples were physically degraded by the high doses of radiation. After 60 kGy the gel separated into two phases. Therefore, the gel samples were not studied further.

The previously reported G value of 2.34 for cerous is significantly lower than the value of 15.6 for ferric. As the cerous R₁ relaxivity is 0.028 s⁻¹mM⁻¹ compared to the relaxivity for ferric (Fe³⁺) of 8 s⁻¹mM⁻¹, the NMR dose response of cerous is lower. The calculated theoretical dose response using the reported G value and relaxivity data for the ceric solution is 0.0068 s⁻¹kGy⁻¹ which is in close accordance with our results. The previous predicted dose response is thus one order of magnitude to large.

The reason for the non-linearity above 40 Gy is most likely due to the great sensitivity to impurities and the problem associated when using small samples. The hydrogen and hydroperoxy radicals and hydrogen peroxide molecule act in the ferrous sulfate dosimeter as oxidation species but in the ceric solution they act as reduction species as follows:

Ce⁴⁺ + H → Ce³⁺ + H⁺
Ce⁴⁺ + HO₂ → Ce³⁺ + H₂O₂ + O₂
Ce⁴⁺ + H₂O₂ → Ce³⁺ + H⁺ + HO₂

whereas the hydroxyl radicals still act as oxidation species:

Ce³⁺ + OH → Ce⁴⁺ + OH⁻

To decrease the actual relaxation rate at high doses this reaction and other oxidation processes must dominate. As heating of the samples at higher doses was significant, this may further promote these reverse reactions and thus lower the actual cerous concentration.

Conclusions
The ceric sulfate dosimeter has potential for high dose NMR dosimetry. The limitations discovered in this study make it unlikely that a ceric sulfate gel dosimeter can be developed.

References