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Sonochemical dosimetry: A comparative study of Weissler, Fricke and terephthalic acid methods

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ABSTRACT

Acoustic cavitation and sonochemical reactions play a significant role in various applications of ultrasound. A number of dosimetry methods are in practice to quantify the amount of radicals generated by acoustic cavitation. In this study, hydroxyl radical ($OH^{\bullet}$) yields measured by Weissler, Fricke and terephthalic acid dosimetry methods have been compared to evaluate the validities of these methods using a 490 kHz high frequency sonochemical reactor. The $OH^{\bullet}$ yields obtained after 5 min sonication at 490 kHz from Weissler and Fricke dosimetries were 200 μM and 289 μM, respectively. Whereas, the $OH^{\bullet}$ yield was found to be very low (8 μM) when terephthalic acid dosimetry was used under similar experimental conditions. While the results agree with those reported by *Iida et al.* (Microchem. J., 80 (2005) 159), further mechanistic details and interfering reactions have been discussed in this study. For example, the amount of $OH^{\bullet}$ determined by the Weissler and Fricke methods may have some uncertainty due to the formation of $HO_2^{\bullet}$ in the presence of oxygen. In order to account for the major discrepancy observed with the terephthalic acid dosimetry method, high performance liquid chromatography (HPLC) analysis was performed, where two additional products other than 2-hydroxy terephthalic acid were observed. Electrospray ionization mass spectrometry (ESI-MS) analysis showed the formation of 2,5-dihydroxyterephthalic acid as one of the by-products along with other unidentified by-products. Despite the formation of additional products consuming $OH^{\bullet}$, the reason for a very low $OH^{\bullet}$ yield obtained by this dosimetry could not be justified, questioning the applicability of this method, which has been used to quantify $OH^{\bullet}$ yields generated not only by acoustic cavitation, but also by other processes such as γ-radiolysis. The authors are hoping that this Opinion Paper may initiate further discussion among researchers working in sonochemistry area that could help resolve the uncertainties around using these dosimetry methods.

1. Introduction

Chemical and physical effects of acoustic cavitation are well-explored concepts in ultrasonic research [1]. In 1927, Wood and Loomis [2] reported a preliminary survey of the chemical effects of ultrasound, initiating significant follow up research on the chemical effects of ultrasound [3–20]. Cavitation-induced dissociation of water molecules into hydroxyl radicals ($OH^{\bullet}$) and hydrogen atoms/radicals ($H^{\bullet}$) and their diverse applications are well-established in various fields [12]. High frequency (>200 kHz) ultrasonic reactors have been successfully implemented for various applications such as the synthesis of bio-functional nanoparticles [17], ultrasonic degradation of organic pollutants [18], generation of nitric oxide (NO) for ultrasonic vascular dilation [19] and transcranial sonothrombolysis [20].

The sonochemical efficiency (SE) of an ultrasonic reactor is commonly evaluated by measuring the yield of $OH^{\bullet}$. Several dosimetry methods have been developed for the quantification of $OH^{\bullet}$ generated by acoustic cavitation. Weissler reaction [21,22], TPPS (porphine tetra(p-phenylsulfonate) [1,23], Fricke [24], salicylic acid [25], terephthalate acid [26] and electron spin trapping [26] have been reported as possible

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options for radicals determination methods in the literature. The most commonly used methods are Weissler (potassium iodide, KI), Fricke and terephthalate acid (TA). Table 1 provides an idea of dosimetry results reported in selected studies where two or more methods are compared.

The purpose of providing this comparison table is not to focus on the yields reported by various studies, but to focus on the method-dependent yields reported in each study. It can be seen from Table 1 that the results of these chemical dosimetries have been inconsistent from the genesis. For example, Koda *et al.* [1] reported that the OH• yield measured by Weissler and Fricke methods are similar, within experimental errors, for three different frequencies. Wu and Shi [27] have reported that the rate of formation of H_2O_2 at 20 kHz by the Weissler method was ~ 2.8 μM min^{-1}, whereas the rate of radical formation for Fricke dosimetry under similar experimental conditions was approximately ~ 1.8 μM min^{-1}. This study claimed Fricke dosimetry as a reliable method. Price and Lenz [28] have reported that terephthalic acid dosimetry is much more useful than Fricke system, since it is specific for the hydroxyl radicals and 2–3 orders of magnitude more sensitive than Fricke system. In contrast, Iida *et al.* [22] demonstrated that the *G* (sonochemical efficiency) value of Fricke dosimetry (~13 × 10^{-10} mol J^{-1}) is in reasonable agreement with that of the Weissler dosimetry (~11 × 10^{-10} mol J^{-1}). However, the terephthalic acid (TA) dosimetry yielded a lower *G* value (0.5 × 10^{-10} mol J^{-1}). The reason for such a low *G* value was due to a lower yield of 2-hydroxyterephthalic acid [22]. Similar results [24,29] were reported showing a lower OH• yield by TA dosimetry compared to other dosimetries. The above discussion provides a mixed message on the reliability of different dosimetry methods.

Considering the importance of quantification of radical yields for various chemical and biomedical applications of ultrasound, it is critical to understand the fundamental mechanisms involved in various dosimetries. The current work is focused on the comparison of the radical yields obtained from the Weissler, Fricke and terephthalic acid dosimetry methods not only to ensure the applicability of the measurements in sonochemical processes, but also to evaluate the mechanism and to identify "pros and cons" of each method. In addition, by disseminating these results and discussion as an Opinion Paper, we hope to initiate discussion among sonochemists that may lead to a reliable procedure to quantify cavitation efficiency (*G*).

Table 1
Selected reports on dosimetry results obtained from the Weissler, Fricke, and TA methods.

Frequency in kHz (Applied Power), Dissolved gas	Method			Ref.
	Weissler [OH•] = [2 × I_3^-]	Fricke [OH•] = [Fe^{3+}]	TA [OH•] = [HTA*]	
200 (140–200 W), Air	~ (8 × 10^{-10} × 2) ~16 × 10^{-10} mol J^{-1}	~15 × 10^{-10} mol J^{-1}	–	[1]
400 (120 W), Air	~ (8 10^{-10} × 2) ~16 × 10^{-10} mol J^{-1}	~19 × 10^{-10} mol J^{-1}	–	
500 (10–40 W), Air	~ (7 × 10^{-10} × 2) ~ 14 × 10^{-10} mol J^{-1}	~ 20 × 10^{-10} mol J^{-1}	–	
130 (100 W), Air	(5.5 × 10^{-10}) ~ 11 × 10^{-10} mol J^{-1}	~ 13 × 10^{-10} mol J^{-1}	0.5 × 10^{-10} mol J^{-1}	[22]
20 (450 W), Air	~ (1.4 × 2) ~ 2.8 μM min^{-1}	~1.8 μM min^{-1}	–	[27]
321 (100 W), Air	–	~ 33 × 10^{-10} mol J^{-1}	~ 5 × 10^{-10} mol J^{-1}	[24]
20 (15.8 W), O_2	~ 0.41 μM min^{-1}	–	~ 0.07 μM min^{-1}	[29]
40 (13.5 W), O_2	~ 0.66 μM min^{-1}	–	~ 0.06 μM min^{-1}	
80 (1.05 W), O_2	~ 3 μM min^{-1}	–	~ 0.35 μM min^{-1}	
500 (39.0 W), O_2	~ 27 μM min^{-1}	–	~ 2.7 μM min^{-1}	
300 (25.6 W), Air	~ 4 μM min^{-1}	~ 4.4 μM min^{-1}		

*Hydroxyterephthalic acid.

2. Materials and methods

2.1. Reagents

All chemicals were of AR grade and used as received. Sodium hydroxide (NaOH), potassium hydrogen phthalate ($KHC_8H_4O_4$) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}·4H_2O$) were obtained from Ajax Chemicals. Potassium iodide (KI), ferrous ammonium sulfate hexahydrate ($FeSO_4.(NH_4)_2SO_4·6H_2O$), sodium chloride (NaCl), sulphuric acid (H_2SO_4), terephthalic acid ($C_8H_6O_4$), disodium hydrogen phosphate ($Na_2HPO_4·7H_2O$), sodium dihydrogen phosphate ($NaH_2PO_4H_2O$), and 2-hydroxyterephthalic acid ($C_8H_6O_5$) were purchased from Sigma Aldrich.

2.2. Weissler dosimetry

The concentration of hydrogen peroxide (from which the OH• yield was calculated) was measured by using the colorimetric method described in previous reports [13,21,22]. A Varian Cary 50 Bio UV–visible spectrophotometer was used for the measurement of absorbance of the triiodide complex at 350 nm (the molar absorptivity, ε: 26,400 M^{-1} cm^{-1}) [13,30]. 1 ml of the freshly prepared potassium iodide reagent A (0.4 M KI, 0.05 M NaOH, 1.6 × 10^{-4} M $(NH_4)_6Mo_7O_{24}·4H_2O$) and 1 ml of reagent B (0.1 M $KHC_8H_4O_4$) were mixed with 1 ml of the sonicated water sample and the absorbance was measured.

2.3. Fricke dosimetry

0.392 g $FeSO_4(NH_4)_2SO_4·6H_2O$ (1.0 × 10^{-3} M), 41.1 g 96% H_2SO_4 (0.4 M) and NaCl (0.0585 g, 1.0 × 10^{-3} M) were dissolved in 15 ml of distilled water and mixed well. This solution was made up to 1 L and stored at 4 °C. The absorbance of the Fe^{3+} present in the sonicated sample was measured at 304 nm (ε = 2,197 M^{-1} cm^{-1}) by using a Varian Cary 50 Bio UV–visible spectrophotometer [22].

2.4. Terephthalic acid dosimetry

Terephthalic acid solution was prepared as described by Iida *et al.* [22]. TA (0.33 g, 2 × 10^{-3} M) and sodium hydroxide (0.20 g, 5 × 10^{-3} M) were added to the phosphate buffer (pH: 7.4) prepared from KH_2PO_4 (0.58 g, 4.4 × 10^{-3} M) and Na_2HPO_4 (0.98 g, 7.6 × 10^{-3} M) and dissolved by continuous mixing. The solution was then made up to 1 L by adding distilled water and stored at 4 °C in dark to avoid any photochemical reactions. Emission spectra of the sonicated samples were recorded with excitation and emission wavelengths set at 310 nm and 425 nm, respectively by using a Shimadzu RF-5301PC fluorescence spectrophotometer equipped with a xenon lamp and 1.0 cm optical length quartz cell.

2.5. Ultrasonic reactor

The sonicator used in the experiment was a 358/1,062 kHz dual frequency unit (ELAC Nautic RF generator type LVG 60 A (Kiel, Germany) and operated in a continuous mode. The volume of water inside the sonicator was 250 ml for each experiment and the temperature was maintained at the range of 15–20 °C by using a cooling jacket with ice-cold water circulating in it. Sample solutions (5 ml) were taken in a glass

vial and immersed in the water present in the sonication reactor. Experiments were performed systematically to evaluate the effects of sonication time at varying sonication (applied as indicated by the amplifier) power (10–60 W) and sonication times (5–30 min).

2.6. HPLC analysis

For the HPLC analysis, an Agilent 1260 HPLC system with Agilent Poroshell 120, EC-C18, 3.0 × 50 mm, 2.7 μm column was used. De-aerated distilled water containing orthophosphoric acid buffer (pH 2.04) was used as solvent A and methanol as solvent B. The flow rate was 0.8 ml min^{-1}, the injection volume was 2 μl, and the total run time was 7 min. A gradient of the solvents A and B was used: 1–1.5 min 90/10, 1.5–3 min 80/20, 3–5 min 70/30 and 5–7 min 40/60. A combination of both diode array detector (DAD: 350–390 nm) and fluorescent detector (FLD: The excitation and emission wavelengths were 309 and 412 nm, respectively) were used for quantifying the parent and product species.

3. Results and discussion

Weissler dosimetry: In this method, OH• yield is measured by quantifying the amount of H_2O_2 produced by sonication of water. OH• generated within the cavitation bubbles (Reaction 1) combine to form H_2O_2 (Reaction 2), which then oxidises iodide ions to generate molecular iodine (Reaction 4). I_2 with an excess of I^- forms triiodide complex anion (I_3^-) (Reaction 5) [13,26,31]. The triiodide yield corresponds to the yield of H_2O_2 which can be measured from the absorbance at 350 nm (ε = 26,400 $M^{-1}cm^{-1}$). The amount of OH• yield can be determined by doubling the yield of I_3^- or H_2O_2.

$$H_2O)))\ H^\bullet + OH^\bullet \quad (1)$$

$$2\ OH^\bullet \rightarrow H_2O_2 \quad (2)$$

$$2H^\bullet \rightarrow H_2 \quad (3)$$

$$H_2O_2 + 2\ I^- \rightarrow I_2 + 2\ OH^- \quad (4)$$

$$I_2 + I^- \rightarrow I_3^- \quad (5)$$

Fig. 1 shows the OH• yield measured using the Weissler method. An increase in OH yield with an increase in sonication time and sonication power can be observed.

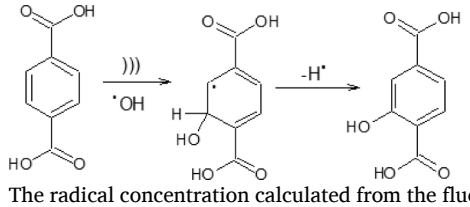
Fricke dosimetry: Fricke dosimetry depends upon the fact that OH• (Reaction 1) and H_2O_2 (Reaction 2) formed due to the sonolysis of water oxidise ferrous (Fe^{2+}) in to ferric (Fe^{3+}) ions (Reactions 6 and 7). H_2SO_4 was added to prevent the oxidation of Fe^{2+} by air, as dissolved oxygen can act as a catalyst for this reaction.

$$OH^\bullet + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O \quad (6)$$

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O + OH^\bullet \quad (7)$$

Fig. 2 shows the results obtained for Fricke dosimetry system. An increase in OH• yield with sonication time and sonication power, similar to that of Weissler method, can be observed.

Terephthalic acid (TA) dosimetry: Terephthalate dosimetry is based upon the hydroxylation of terephthalic acid (TA) by OH•. The product of this reaction, 2-hydroxyterephthalate ion (HTA), is highly fluorescent. Although the major product is 2-hydroxy terephthalic acid, the potential formation of 2,5-dihydroxy terephthalic acid, as well as ipso attack of OH• cannot be ignored [26,32], which will be discussed later. The reaction mechanism for the formation of HTA is shown in Reaction 8.



The radical concentration calculated from the fluorescence emission values of sonicated aqueous TA solution show time and intensity-dependent linear increase (Fig. 3).

Comparison of Weissler, Fricke and TA methods: Fig. 4 shows a comparative picture of the OH• yields measured using the three dosimetry methods.

In order to get further insight, the data presented in Fig. 4 were further processed. The OH• yields in Fig. 4a for 10 min were converted into per minute yield and further divided by the power (40 W) to get OH• yields per minute per unit power and presented in Table 2. The OH• yields in Fig. 4b for 30 W were converted into per unit power (W) and further divided by time (3 min) to get OH• yields per minute per unit power and presented in Table 2.

The following major observations could be identified from Fig. 4 and Table 2:

- The OH• yields measured by all three methods are generally found to increase linearly with an increase in sonication time and power. The OH• yields measured by the Weissler method seems to deviate from linearity at longer sonication times and higher power. A similar trend can be noticed for TA method as well (Fig. 3).
- The OH• yields measured by the Weissler (1.2–1.4 μM min^{-1} W^{-1}) and Fricke (0.96–1.2 μM min^{-1} W^{-1}) methods are similar, within experimental errors, at least until 10–15 min sonication time and 20–30 W applied power.

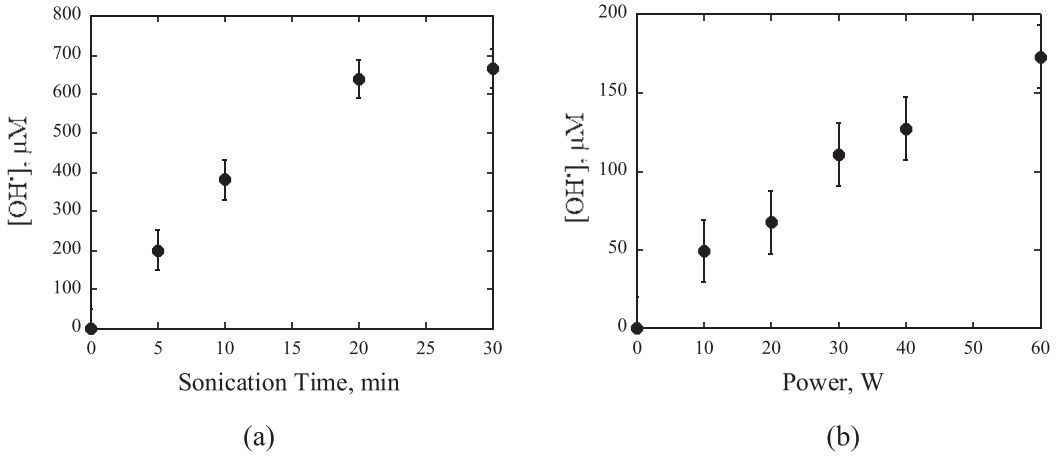


Fig. 1. [OH•] yield measured using Weissler method at 490 kHz as a function of sonication time at a fixed power of 40 W (a) and sonication power at a fixed sonication time of 3 min (b).

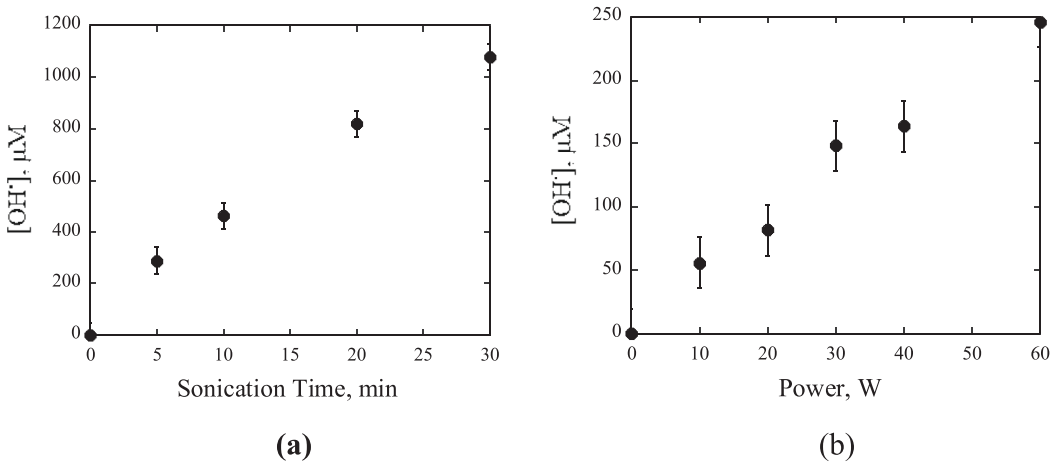


Fig. 2. [OH•] yield measured using Fricke method at 490 kHz as a function of sonication time at a fixed power of 40 W (a) and sonication power at a fixed sonication time of 3 min (b).

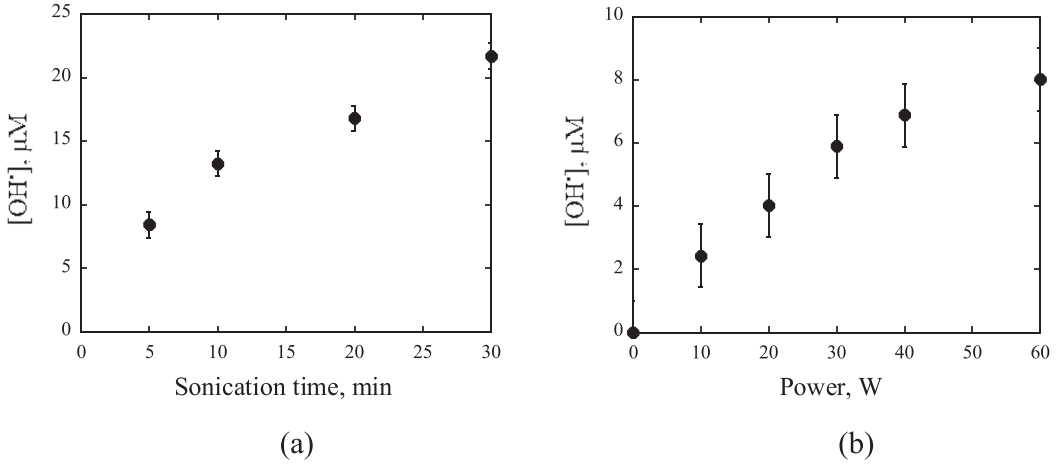


Fig. 3. [OH•] yield measured using TA method at 490 kHz as a function of sonication time at a fixed power of 40 W (a) and sonication power at a fixed sonication time of 3 min (b).

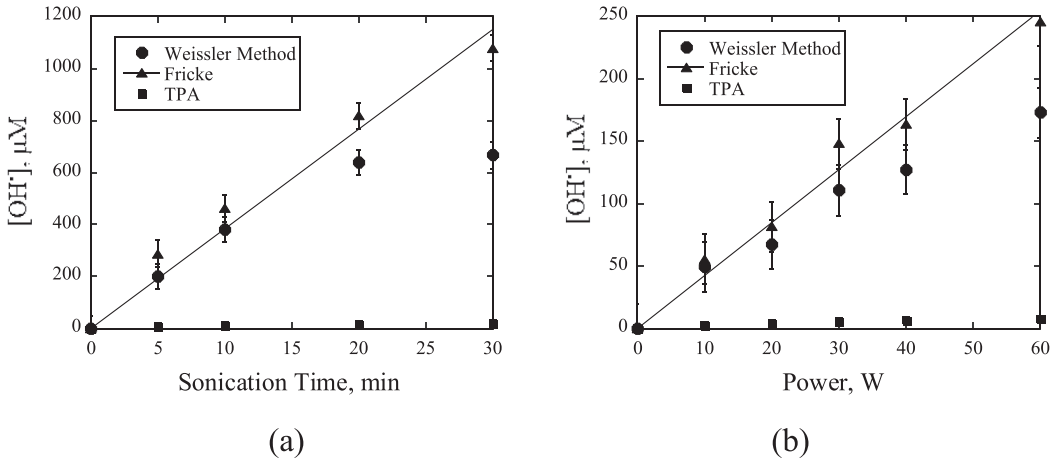


Fig. 4. [OH•] yield measured using all three methods at 490 kHz as a function of sonication time at a fixed power of 40 W (a) and sonication power at a fixed sonication time of 3 min (b).

- The OH• yields measured by TPA (0.04–0.07 μM min^{-1} W^{-1}) method are significantly lower than those measured by the other two methods.

Let us discuss these observations of each method. Since the overall radical yield depends upon sonication time and power, a linear increase in OH• concentration observed with an increase in sonication time and power is an expected outcome, as shown in earlier reports [1,22]. Both

Table 2
A comparison of OH• yield obtained from three methods.

Method	OH• yield Using Data from Fig. 4a		OH• yield Using Data from Fig. 4b	
	μM min^{-1} (40 W)	μM min^{-1} W^{-1}	μM W^{-1} (3 min)	μM min^{-1} W^{-1}
Weissler	48	1.2	4.2	1.4
Fricke	38	0.96	3.7	1.2
TPA	1.4	0.04	0.2	0.07

these parameters (time and power) increase the overall cavitation events. The deviation from linearity at longer sonication time and power is also an expected trend. When considering the Weissler method, H_2O_2 is relatively an unstable product. Over a period of sonication time, it can decompose to form H_2O and O_2. Similarly, in the TA method, the decomposition products could accumulate within the cavitation bubbles and reduce the overall OH• yield due to the lowering of bubble temperature. This is a proven fact at high ultrasonic frequencies where bubbles undergo stable (repetitive transient) cavitation [33]. When using these dosimetries, caution should be taken not to sonicate for long period of times. Ideally, less than 15 min of sonication time and moderate power levels (10–40 W under the experimental conditions used in this study) are needed when using these methods to quantify acoustic cavitation yields.

OH• yields measured by the Weissler and Fricke dosimetry methods are similar, within experimental errors. A similar observation is reported in previous studies (Table 1). While this observation may suggest that these are reliable methods, one should be aware of some complexities involved in these methods. For example, in air-saturated water, H• generated within cavitation bubbles could be converted into HO_2• radicals and ultimately to H_2O_2 (Reactions 9 and 10).

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad (9)$$

$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (10)$$

Whether the formation of additional H_2O_2 would contribute to an increase in measured OH• yield by Weissler method is questionable. Similarly, in air-saturated water, •HO_2 (Reaction 9) may also oxidise Fe^{2+} to Fe^{3+} (Reaction 11), which could provide unreliable OH• yield.

$$HO_2^{\bullet} + Fe^{2+} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \quad (11)$$

Having said this, the amount of H_2O_2 produced through Reactions 9 and 10 could be negligible or significant to provide a higher OH• yield than expected in both methods. An obvious experiment to do is to carry out these reactions in an inert (oxygen free) solution and compare the results with those observed in air saturated solutions.

The radical yield obtained from TA dosimetry is significantly less than that obtained from the other two methods. A similar observation was reported by Iida *et al.* [22]. It is also known from a number of previous studies that looked into utilising cavitation generated OH• for the degradation of organic pollutants in aqueous media that reaction of OH• with aromatic molecules generate multiple products. For example, the sonication of phenol generated di- and tri-hydroxylated products that ultimately can be converted into aliphatic carboxylic acids on continuous sonication [34]. Considering this, the reliability of TA dosimetry on the formation of a single hydroxylated product needs to be validated.

Earlier reports on HPLC analysis of terephthalic acid dosimetry have shown only mono-hydroxylated products [35–37]. We have performed a thorough investigation of the products generated from TA during sonication. A HPLC method using Poroshell 120 EC-C18 column was developed for the analysis of the products of the reaction between OH• and TA. HPLC chromatograms in Fig. 5 shows the products obtained after 30 min sonication of TA solution. HPLC chromatograms of TA and HTA standards are also shown for comparison purposes.

The major peaks at RT (retention time) of 0.8 min and 3.2 min correspond to 2,5-dihydroxy terephthalic acid and 2-hydroxy terephthalic acid respectively, which were further confirmed by ESI-MS analysis. A plot of peak area *vs* sonication time shows the time dependant linear increase in the formation of 2,5-dihydroxy terephthalic acid as well as 2-hydroxy terephthalic acid. Interestingly, a new peak was also found at a RT of 3.1 min, the molecular weight of which was not detected by the ESI-MS protocol used. Hoffmann and co-workers [29] have also noted that interpretation of the apparent rate constants for hydroxyl radical production may be complicated by several factors. First, terephthalic acid must diffuse to the bubble surface in order to trap OH•. Hydroxyterephthalic acid (HTA), formed at the interface may react further with OH• before it diffuses away from the bubble surface. Therefore, quantifying OH• yield via hydroxyterephthalic acid represents a lower limit of OH• production rate under a given set of conditions. HPLC and ESI-MS data also showed that the peak area of TA did not decrease significantly even after 30 min of sonication supporting the above discussion that OH• were not efficiently 'quenched' by TA.

Attempts were made to quantify di-hydroxylated product (RT) and unidentified products observed in the HPLC chromatogram and ES-MS. However, these products did not account for the significantly lower yield of OH•, measured by the TA dosimetry method. The question on the reliability of this method remains open despite the higher sensitivity of this method to detect lower yields of OH• by fluorescence technique.

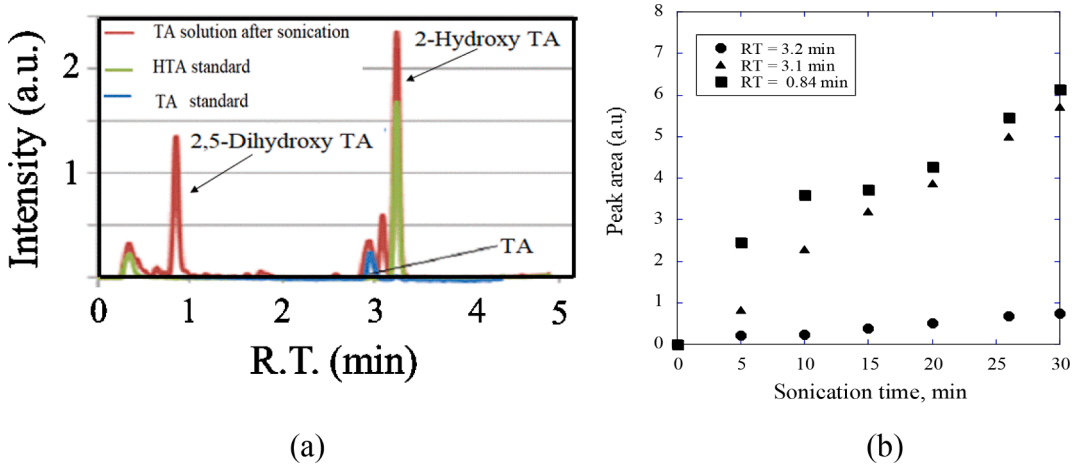


Fig. 5. (a) HPLC chromatograms of standard HTA, TA and sonicated TA solutions; (b) A plot on HPLC-Peak areas *vs.* sonication time. Major peaks at RT (retention time) 3.2 min and 0.84 min correspond to 2-hydroxyterephthalic acid and 2,5-dihydroxyterephthalic acid (identified using standards and ESI-MS), respectively.

4. Conclusions and questions for further discussion and future investigations

The current study has clearly highlighted that the $OH^{\bullet}$ yields measured by the Weissler and Fricke dosimetries are comparable, as reported in previous studies. However, the question that remains unanswered is the reliability of these methods due to the involvement of $HO_2^{\bullet}$ that may lead to an overestimation of the amount of $OH^{\bullet}$ generated during sonication. As mentioned in the discussion, repeating these experiments under inert atmosphere (e.g. Ar, N_2, etc.) may provide further insight on this issue. The authors intend to work on these experiments and share the outcome in a follow-up discussion paper.

The results presented herein clearly indicate that the sonochemical yield measured by the TA dosimetry method is significantly lower compared to that measured by the Weissler and Fricke dosimetries, confirming *Iida et al.*'s earlier report [22]. Our attempt to find out the causes for this difference by detailed HPLC and ESI-MS analysis did not provide a possible solution to this issue. While the formation of additional hydroxylated products was identified, it did not account for the significant lower yield measured by this method compared to that measured by other methods.

One final remark the authors would like to make is the reliability of any dosimetry method for quantifying cavitation activity. Henglein [38], in one of his early studies mentioned that about 80% of the primary radicals recombine within cavitation bubbles and only 20% are involved in redox reactions. It has been shown [39] that surface active solutes can be used to minimise the recombination of primary radicals and maximise secondary reducing radicals. The surface-active solutes, by adsorbing at bubble-solution interface, may quench these radicals before they can recombine. Based upon such observations, the applicability of Weissler, Fricke and TA dosimetry methods for quantifying cavitation efficiency can also be questioned.

Irrespective of such uncertainties, these dosimetry methods do provide some way of quantifying the cavitation efficiency when experimental parameters such as sonication time, power, frequency, solute concentration, etc. are varied. Individual dosimetry methods can be used for comparing relative yields when varying a single experimental parameter.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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