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Towards the understanding of a complex cavitation environment – electrochemistry, acoustics and imaging observations

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Abstract

A set of experiments designed to characterize an ultrasonic reactor are presented. These include electrochemical, acoustic and imaging of the reactor deployed. In particular an electrochemical technique, that can detect the erosion caused by single inertial cavitation events within an ultrasonic reactor, is reported. The technique relies on the erosion/corrosion of an electrode surface. The sensitivity of the technique is discussed in relation to normal weight loss measurements. In order to operate this system an opto-isolation approach is discussed which enables the electrochemical measurements to be undertaken within an earthed metallic ultrasonic bath. Mapping of the reactor is combined with luminescent imaging.

Keywords: erosion, corrosion, luminescence, mapping.

1 Introduction

The ultrasonic environments where cavitation is produced are complex [1, 2]. These environments are dynamic in nature with the formation and destruction of bubbles and bubble clouds complicated by the acoustic interaction between the sound field employed and objects within the media [3]. In addition the cavitation bubbles themselves contribute to the sound field in adding complexity and local effects. As a consequence many different analytical techniques have been employed to investigate these environments [4]. For example, the measurement of pressure distributions, optical imaging both using high-speed cameras and image intensified systems as well as monitoring chemical effects have all been

employed to try and characterise the system [5-7]. In addition electrochemical techniques have been deployed to follow mass transfer effects and surface erosion produced by the environment [1, 8-14]. In this case it should be noted that these electrochemical techniques target different mechanisms within the environment. For example mass transfer of material is dependant on many factors including acoustic streaming, microstreaming [15-17], jetting and bubble motion. These may be associated with inertial [18] and non inertial cavitation processes as well as the reactor geometry itself. However, surface erosion is more restrictive relying on the removal of material from a surface which is often linked to inertial collapse close to the solid/liquid interface. Nevertheless, whatever technique is employed, advantages and disadvantages should be noted [4]. In the following discussion, an electrochemical erosion/corrosion sensor is further investigated and used to probe an operating ultrasonic bath.

2 Experimental

Electrochemical measurements were performed using a two electrode arrangement. An aluminium electrode (250 μm diameter, Advent Research materials) working electrode sealed in an epoxy support (~ 2 mm diameter) and a silver or stainless steel reference counter electrode was employed. The potential of the aluminium electrode versus the exact reference employed is shown in the appropriate figure legend. The surface of the working electrode was polished to a mirror like finish using 0.3 μm alumina on a polishing pad. The current passed at the working electrode was monitored using a simple in-house current follower or a bespoke optocoupled current follower (details described elsewhere [19]). The data from each device was recorded using an ADC card (Measurement computing) or a Le Croy 9310 digital oscilloscope. Event counting was achieved using in-house written software (VB 6) or an Amptek Pocket MCA 8000A. Ultrasound was produced by a piston like emitter (Adaptive Biosystems, 3 mm diameter tip) operating at ~ 23 kHz. This device was driven by a B&K 2713 power amplifier supplied with a signal by a function generator (TTi). In addition a standard ultrasonic bath was also employed (Ultrawave U50).

A Darkstar intensified CCD video camera from Photonics Science was used to capture images of luminol emission. A Photron APX RS high-speed camera with a Navitar 12x lens was used to record the high speed images.

Sodium sulphate (Fisher, LRG), 3-Aminophthalhydrazide (Luminol, Aldrich, 97 %), hydrogen peroxide (BDH, 29-31 %), sodium carbonate (BDH, 99 %) and EDTA (Lancaster) was used as received, the exact concentration is reported in the appropriate figure legend. Water was supplied by a Purite Select Fusion 160 (Ondeo) water purification system (resistivity typically >15 M Ω cm and a TOC < 10 ppb). Solutions were aerobic and at 20-24 $^{\circ}\text{C}$.

3 Results

Figure 1 shows the methodology adopted for the electrochemical erosion/corrosion measurements. In this system the erosion of the surface is initiated by a mechanical effect on the passive layer. This may originate from cavitation or from particle impact. However, the erosion of the passive layer (here an aluminium surface under passive conditions) discussed here is initiated by a cavitation effect. This may be associated with bubble collapse, cluster collapse, bubble jetting and shock emission. Figure 1(a) shows the surface

in a passive state prior to this erosion. In this state no current is observed. In the presence of a suitable erosive mechanism (here cavitation), the passive film is removed (see figure 1(b)). It should be noted that due to the nature of the electrochemical response no current is observed at this exact moment. However, in the subsequent passivation phase electron flow from the surface (an anodic oxidation of the exposed Al surface) is captured by the electrochemical control maintained by the equipment employed. Hence, it is the passivation phase (or corrosion phase) of the process which is recorded (see figure 1(c), (d)). Although this is subsequent to the erosion event itself, it is still rapid on the electrochemical timescale. Erosion transients on the order of 50-100 μs are detected have been detected. This is as the result of careful choice of the electrode material, potential control, electrode area and the solution composition. Finally the surface returns to the passive state ready to detect further erosion.

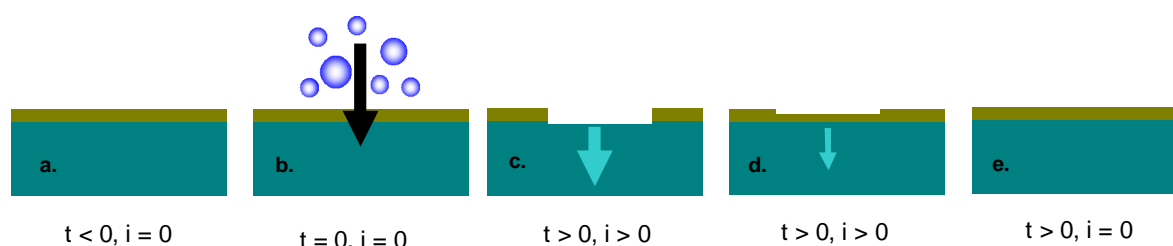


Figure 1. Sequence of events associated with the erosion/corrosion measurements described here. The passive layer on the electrode surface ■ and the underlying electrode substrate ■ are shown. The erosion stage is shown by a black arrow and the electron flow a light blue arrow.

The size of the electrode surface is also important. If the electrode surface is too large, multiple erosion events may be detected. This is not desirable from a sensor perspective. In addition electrochemical limitations will also become important. Figure 2(a) shows a series of erosion/corrosion events detected on an aluminium electrode using the methodology described in figure 1. Here a number of current time transients are shown from continuous cavitation generated in this case by a piston like emitter. Figure 2(a) shows six transients recorded over $\sim 600 \mu\text{s}$, the largest producing a current maximum of $25 \mu\text{A}$. Integration of these current time transients is useful in determining the amount of material eroded in the sequence. Figure 2(b) shows the charge passed as a function of time for this particular sequence. Figure 2(b) demonstrates that for the largest event, $\sim 400 \text{ pC}$ of charge is recorded. In turn, through Faraday's law, this can be converted to an equivalent mass removed from the surface. Figure 2(b) shows that mass changes of the order of 50 fg are removed for the larger erosion/corrosion events while smaller events produce approximately one order of magnitude less charge ($\sim 5 \text{ fg}$). These numbers are significant. Consider other methods of the detection of surface damage. The most popular cavitation erosion assessment method is the measurement of mass loss from a material. Here mass changes on the order of 1 mg are noted [20]. While this is an analytical method several problems can be foreseen. For example in comparison to the erosion/corrosion measurements reported here this is 11 orders of magnitude less sensitive. Some caution should be noted. In order to use the erosion/corrosion method, a number (for example 10^5) of events would normally be detected in a single measurement. Nevertheless, the erosion/corrosion method is still many orders of magnitude more sensitive. Finally, the electrochemical method can be performed *in situ* while mass loss measurements usually rely on assessment of the sample after exposure to cavitation. This may introduce inaccuracies due to liquid removal or parasitic natural corrosion.

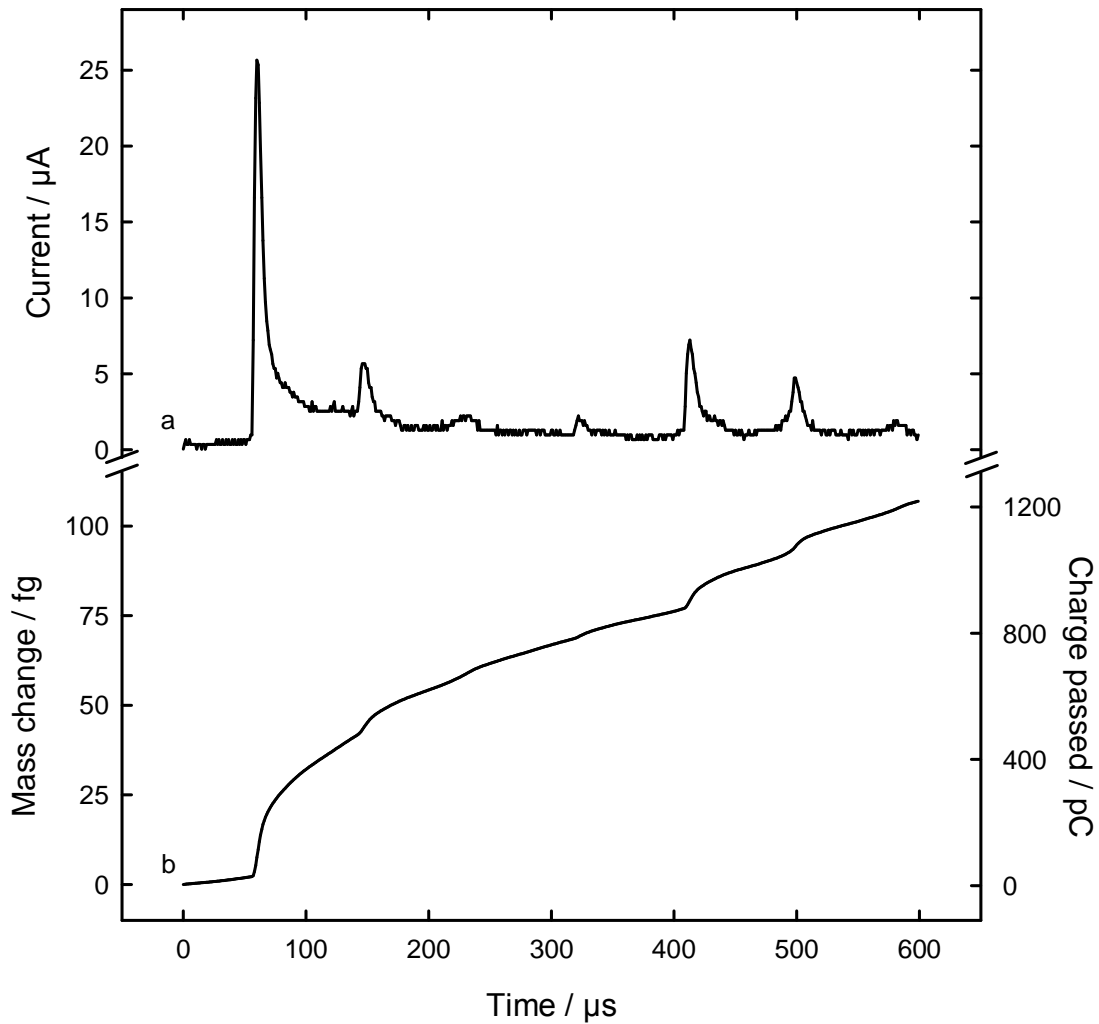


Figure 2. (a) Plot of current as a function of time for a series of surface erosion/corrosion events. (b) Plot of the corresponding charge and calculated mass change. The data was gathered from a 250 µm diameter Al electrode held at 0 V vs. a Ag counter/reference electrode in 0.1 M Na₂SO₄. The electrode was held 0.5 mm away from an ultrasonic horn (3 mm diameter) driven at 23.43 kHz and 100 V zero-to-peak drive amplitude.

Turning to the mechanisms responsible for the erosion of the surface, figure 3 shows an experiment performed combining high-speed imaging and electrochemical measurements. Figure 3 shows a single electrochemical erosion/corrosion transient. The circles represent the positions and exposure time of the high-speed imaging (shown as an insert in figure 3). Prior to the measurement of erosion, a cluster of bubbles can be seen in frames 1-3. However, this is seen to collapse in frame 4 of the high-speed sequence. Immediately after this event has cleared, the electrochemical data shows erosion has occurred as an anodic deviation in the current was observed (see frame 4 and the deviation from zero current).

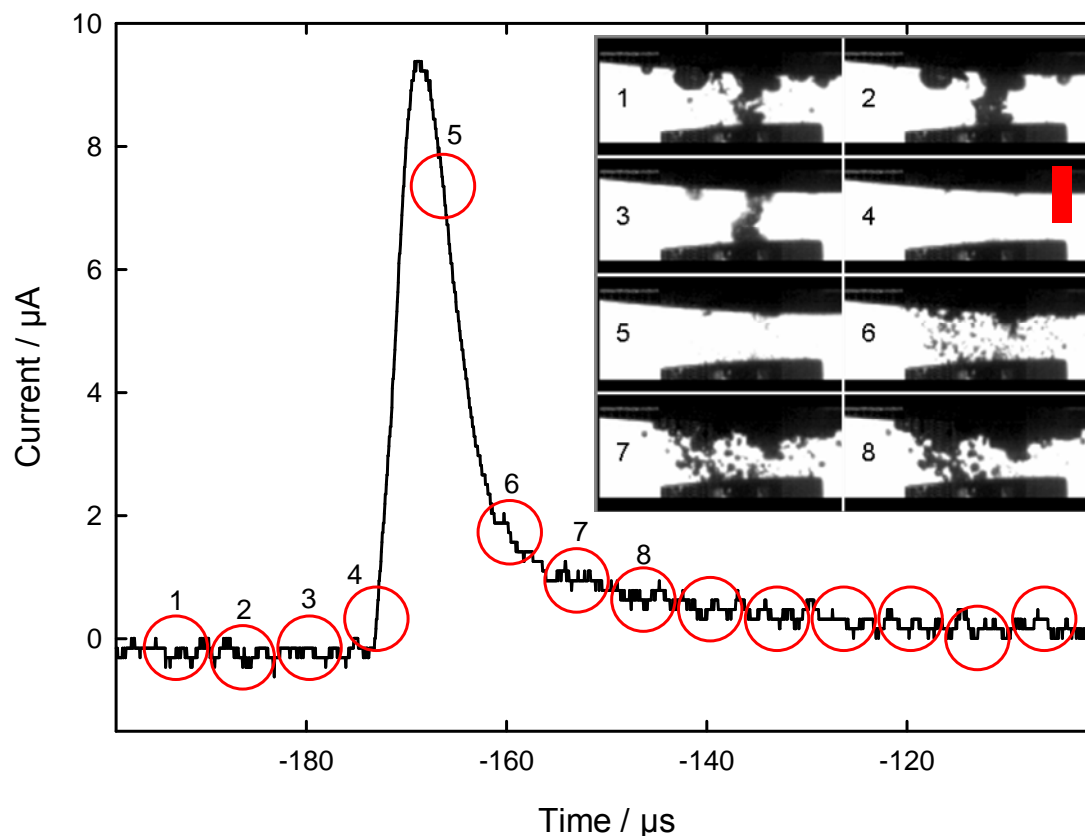


Figure 3. Current time trace of a surface erosion/corrosion event recorded on a 250 μm diameter electrode and simultaneous high-speed video images. The numbered circles on the current time trace represent the duration and timing of the same numbered high-speed images. The event was recorded in 0.1 M Na_2SO_4 with the ultrasonic horn driven at 22.66 kHz and 110 V zero-to-peak. The electrode was positioned 1 mm from the tip of the horn and held at 0 V vs. an Ag counter/reference electrode. The images were recorded at 150,000 frames s^{-1} with a shutter speed of 1/150000 s. The scale bar (frame 4) represents 1 mm.

Interestingly the electrochemical data shows that the erosion/corrosion event has started to diminish before further cavitation bubbles are recorded by the high-speed imaging (see frame 6). This is significant as the electrochemical recovery of the surface is sufficiently fast to be ready for further erosion relatively rapidly on the timescale shown here. This is a particular advantage of this system as it indicates that the electrochemical approach is suitable for multiple erosion/corrosion event detection. Figure 4 shows how this electrochemical method can be used to assess multiple erosion/corrosion events detected from continuous ultrasound. Note in this case the electrode was exposed to continuous ultrasound while the current time transients were recorded using two simultaneous methods. In the first method, the current time data was continuously recorded while in the second the signal was passed to a MCA. Figure 4(b) shows that the analysis of the current time data using in-house written software to detect both the number and size of the current time transients recorded. In this data set most of the events are relatively small ($<10 \mu\text{A}$) while the event frequency decreases as the size of the event decreases. This is understandable as the largest events are detected when both the maximum damage to the passive layer occurs. However, this is the least likely event. In addition it should be noted that the electrode material has little or no influence on the position of the cavitation event.

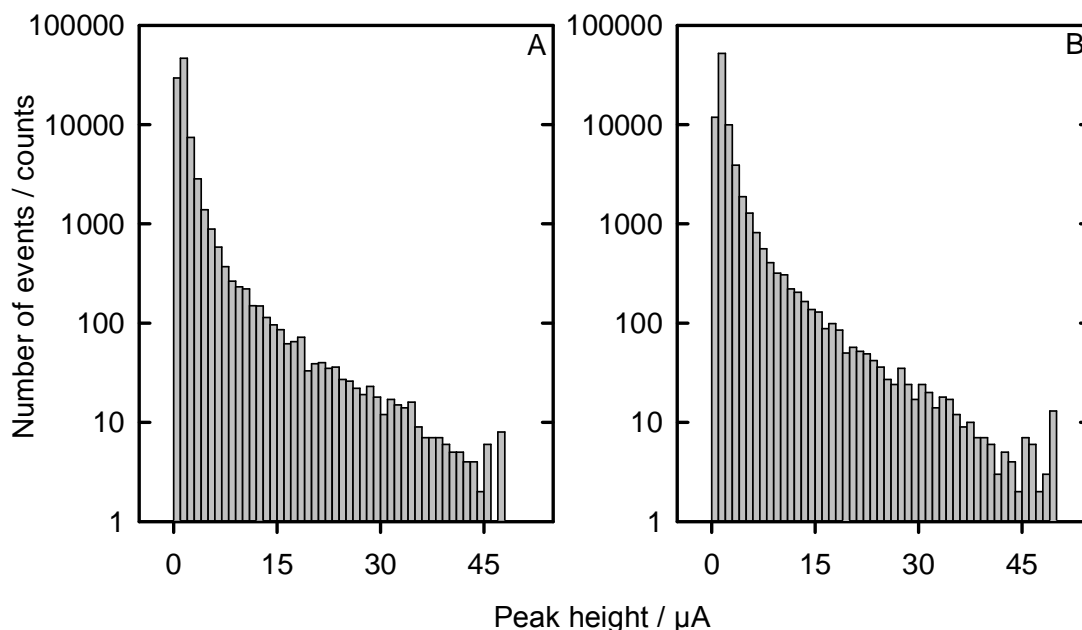


Figure 4. Comparison of the size distribution of events recorded using the MCA (A) and ADC card with software (B) counting techniques.

Hence, the electrochemical data indicates that many events may either not remove the most possible amount of passive layer or not be centred on the electrode surface itself. These more likely events will produce the smaller erosion/corrosion events. Finally, no indication on the mechanistic detail responsible for these events can be obtained from this data. This is beyond the scope of this manuscript and will be discussed elsewhere. Figure 4(a) shows the same current time data set analysed by an MCA. This shows very similar data as the post analysed data set shown in figure 4(b). However, some significant experimental points should be noted. The data set analysed corresponds to a ~250 Mb data file and requires significant post processing. This is due to the significant amount of data and analysis required. However, the MCA approach is in real time and produces data files which are ~ 20 kb. This is clearly four orders of magnitude less and involves considerably less analysis.

While the data shown thus far has demonstrated that the electrochemical erosion approach is useful, it has been employed in one particular environment, the piston like emitter. Although the piston like emitter is a useful tool for sonochemistry, surface analysis and biological sample preparation etc. other reactor geometries should be considered. Here we deploy this electrochemical sensor in an operating ultrasonic bath. In this case the sensor is used to access the effects of other bodies (for example the basket) on the erosion field. However, this environment provides a considerable problem. The earthed metal bath walls provide considerable electrochemical interference. However, this can be avoided through appropriate isolation methods. This has been described elsewhere. Briefly the electrochemical equipment is optically isolated to avoid interference effects. Turning to the cavitation field produced by an operating ultrasonic bath, it is convenient to image this field using the light emission generated by multibubble sonochemiluminescence (MBSCL) [21, 22]. Figure 5(a) shows a view from above of the ultrasonic bath employed here recorded under normal light conditions. Figure 5(b) shows the same bath imaged under blackout conditions using an image intensifier. Here the white regions correspond to light emission through the coupled sonochemical oxidation of luminol in the matrix employed. This is a useful technique as the amplification of light emission over conventional MBSL is up to two orders of

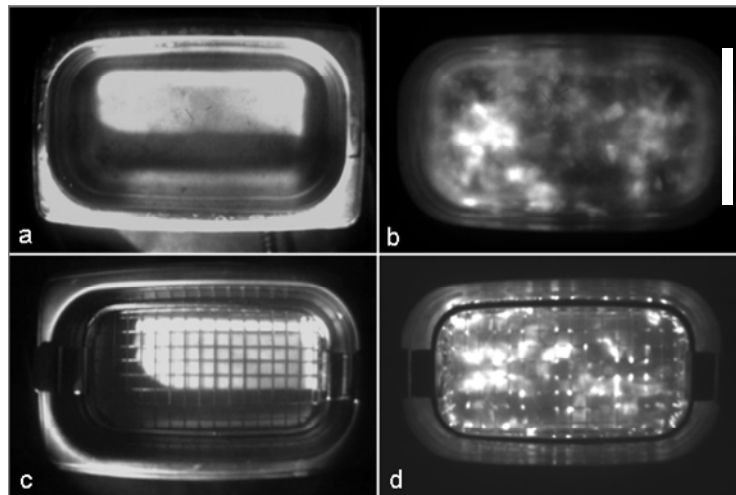


Figure 5. Images showing the change in light emission from bath A unperturbed (b), with the addition of a wire supporting basket (d), with the addition of the basket. Each low light image is a stacked and averaged combination of 101 individual images. The bath contained 500 ml of a solution of 0.1 M Na_2CO_2 , 0.1 mM EDTA and 5 μM luminol. The scale bar (see frame (b)) represents 85 mm.

magnitude[23]. Figure 5(b) shows that cavitation (indicated by white areas in the image) is distributed through the bath although a 'hot spot' can be seen towards the bottom left hand corner of the system. Figure 5(c) shows an image of the same bath recorded under non blackout conditions with the addition of the support basket. Figure 5(d) shows the effect of this basket on the luminescence. The basket can be seen to have a dramatic effect on the luminescence seen from the bath. The luminescence can be seen to concentrate around the wire structure of the basket. This effect can be further investigated by employing the electrochemical erosion/corrosion sensor within an operating ultrasonic bath.

Figure 6 shows the result of mapping erosion/corrosion events within an ultrasonic bath. Figure 6(a) shows mapping within the bath in the absence of a basket. Clearly significant surface erosion can be detected (up to 10^4 in a 30 s period) under these conditions. However, figure 6(b) shows that the addition of the basket (shown as a white grid) on the electrochemical erosion/corrosion measurements. A dramatic loss in surface erosion activity was observed with little or no erosion detected over the scan area. However, one 'hot spot' remains (at 10, 10) with up to 6000 erosion/corrosion events recorded over the 30 s measurement period. This situation is not improved significantly by the addition of other objects to the system. Figure 6(c) shows the addition of a 1p coin to the bath. Although the position of the erosion/corrosion signal has changed, improvement in surface erosion over the entire scan was not observed. In addition the hot spot (now at 10, 3) has reduced in activity (now ~ 60 erosion/corrosion events over the 30 s period). These results are in agreement with the luminescence imaged shown in figure 5. Clearly the addition of objects (including the basket) has a dramatic effect on the surface erosion produced by an operating ultrasonic bath and appears to reduce the surface ability of these systems. This is perhaps not surprising considering the acoustic perturbations that these objects impose on the sound fields but is noteworthy particularly is surface cleaning of objects placed in these baths is required.

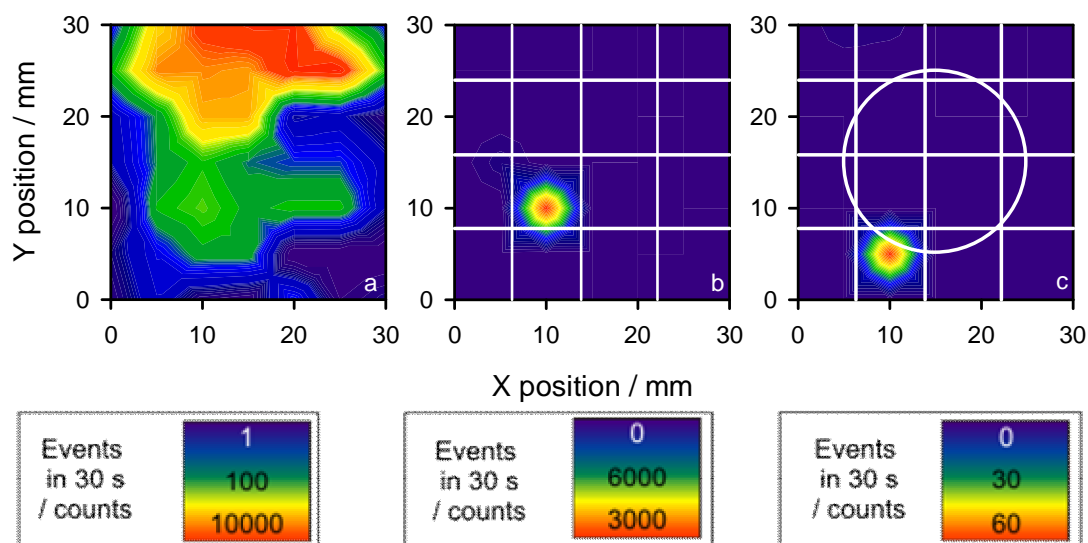


Figure 6. Contour traces showing the distribution of the surface erosion/corrosion activity over a portion of an unperturbed ultrasonic bath (a), in the bath with the addition of the wire support basket (b) and with the addition of the basket and a 1 p coin (c). Scans conducted over a 30 by 30 mm area. Events recorded on a 250 μm diameter Al electrode held at 0 V vs. a SS counter/reference electrode using the MCA collecting over 30 seconds with a threshold of 0.85 μA . The bath contained 2 dm^3 of 0.1 M Na_2SO_4 .

4 Conclusions

The electrochemical erosion/corrosion technique is a powerful method for the assessment of cavitation processes. In particular the technique is many orders of magnitude more sensitive than conventional mass loss methods, can be used to scan erosion fields generated by reactors and can be employed as a probe within the media. High-speed imaging indicates that erosion from a piston like emitter appears to be initiated by the disappearance of bubbles within the media. Finally, the erosion/corrosion method and luminescence imaging show the drastic effects of the insertion of objects within an operating ultrasonic bath.

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