Drop-spark discharge: an atomization and excitation source for atomic emission sensors

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Drop-spark discharge (DSD) arising after breakdown in the air gap between two approaching free electrolyte surfaces may be used as an atomization and excitation source for a new optic sensor.

Despite the well-known advantages of atomic emission spectroscopy (AES) it is not the usual technique for sensors: routine atomization sources are too large and powerful, and nebulizers are too complicated for the purpose. Nonetheless, due to the high selectivity of AES the possibility of making AES sensors is very attractive. In our opinion, low energy electrical discharges on a free water electrolyte surface are promising sources for this goal. In this case a discharge provides both light emission and sample introduction by sputtering of the electrolyte cathode. Cherfalvi and Mezei[1,2] described an analytical application of continuous glow discharge with an electrolyte cathode (ELCAD) and a metal anode. Here we discuss unidirectional discharge in the air gap between a lowering drop and a free water surface. In contrast to ELCAD, drop-spark discharge (DSD) is an impulse source and has no solid/plasma interface.

A discharge cell contains two 2.5 mm i.d. glass tubes, one above the other (see Figure 1). Analysing solution (catholyte) was delivered through the lower tube at a flow rate of *ca*. 3 ml min^{-1}. The anolyte (usually 0.4 M HCl) was added dropwise from the upper tube (3–10 drops per minute). The cell was open to the ambient air. The plates of a 2 μF capacitor were connected with two platinum wire electrodes immersed in catholyte and anolyte, respectively. During discharge the voltage was reduced from 800 V to *ca*. 600 V; a low power high voltage supplier restored the initial value of the capacitor voltage during a few seconds of intermittence. The emission intensity was detected in the range from 370 to 800 nm with two photomultiplier tubes. Spectral selection was achieved with a monochromator for the first one and with a 589 nm interference filter (band pass 2 nm, transmittance 64%) for the second one. Current and light pulses were recorded with a PC data acquisition board. Time resolution was *ca*. 30 μs.

A scheme of drop motion and light/current response are presented in Figure 1. The discharge started when the distance between the lower surface of a drop and the upper surface of liquid in the lower tube became small enough for breakdown. The latter was accompanied by current and light emission pulses. Thereafter, in a few milliseconds the current was almost constant, whereas light intensity (in particular, the Pb 405.8 nm line in Figure 1) strongly oscillated. The circuit was then shorted out by an elecrolyte bridge, leading to a strong increase in current and termination of light emission (step II).

There are at least three kinds of emitters with specific kinetics in DSD: metal atoms, products of water decomposition (H· and HO· radicals) and atmospheric gases. The behaviour of atmospheric gases in DSD is too complex and varied to be described in detail. They create rather intense background emission in the range from 370 to 500 nm. As distinct from other species, N$_2$ and N$_2^+$ bands give a very strong short pulse during breakdown. It is an N$_2$ band with a peak at 405.9 nm that is reponsible for the first peak on the light intensity curve in Figure 1.

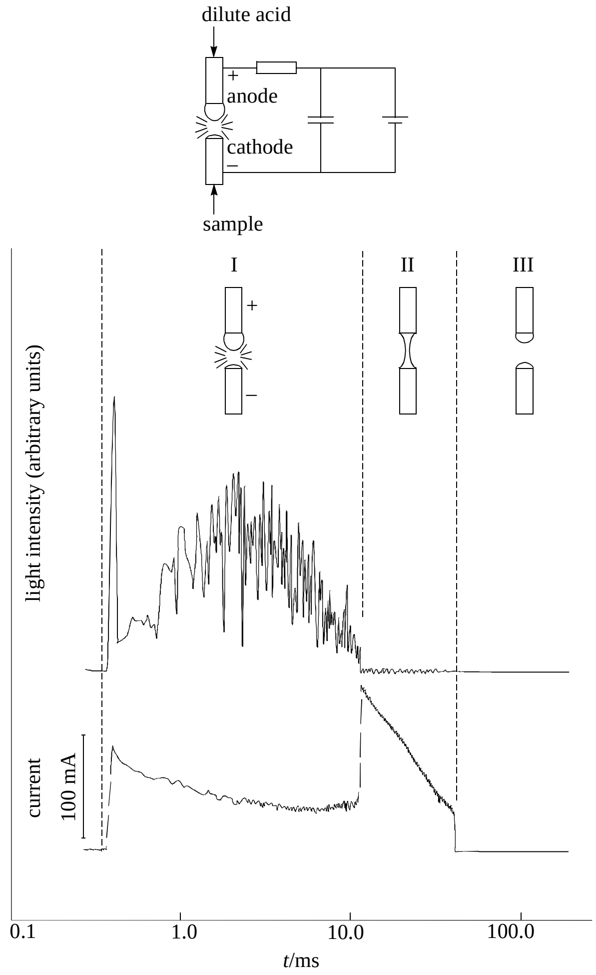

Figure 1 Circuit diagram, steps for drop motion (I – discharge, II – short, III – intermittence) and time dependence of current and light intensity. *Conditions*: 405.8 nm, band pass 2 nm, catholyte 5 mM Pb$^{\mathrm{II}}$ in 0.4 M HCl.

Table 1 Reproducibility of atomic emission intensity, conditions as in Figure 2, *n* = 55.

Integrated intensity	Relative standard deviation, s_r
Na 589 nm	0.048
In 451 nm	0.046
H 656 nm	0.036
Na 589 nm/In 541 nm	0.018
Na 589 nm/H 656 nm	0.048

Only the most intense atomic lines can be used for metal determination with DSD, in particular Na 589.0 and 589.6 nm, Ca 422.7 nm, Pb 405.8 nm, Ga 417.2 nm, K 766.4 and 769.9 nm, In 451.1 and 410.2 nm, Tl 535.1 nm, Mg 516–519 nm, Li 670.8 nm. As Figure 2(*a*) indicates, the intensities of the Na 589 nm and In 451 nm lines pulsed strongly and synchronously, which is common for other metals. The intensity of the H 656, 486 and 434 nm lines do not oscillate as strongly as for metal lines. As Figure 2(*b*) illustrates, there is no obvious correlation between the pulsations of the H 656 nm and Na 589 nm lines. The difference in emission kinetics for metals and hydrogen appears to be connected with the values of the excitation potential. For hydrogen this value exceeds 12 eV while for the

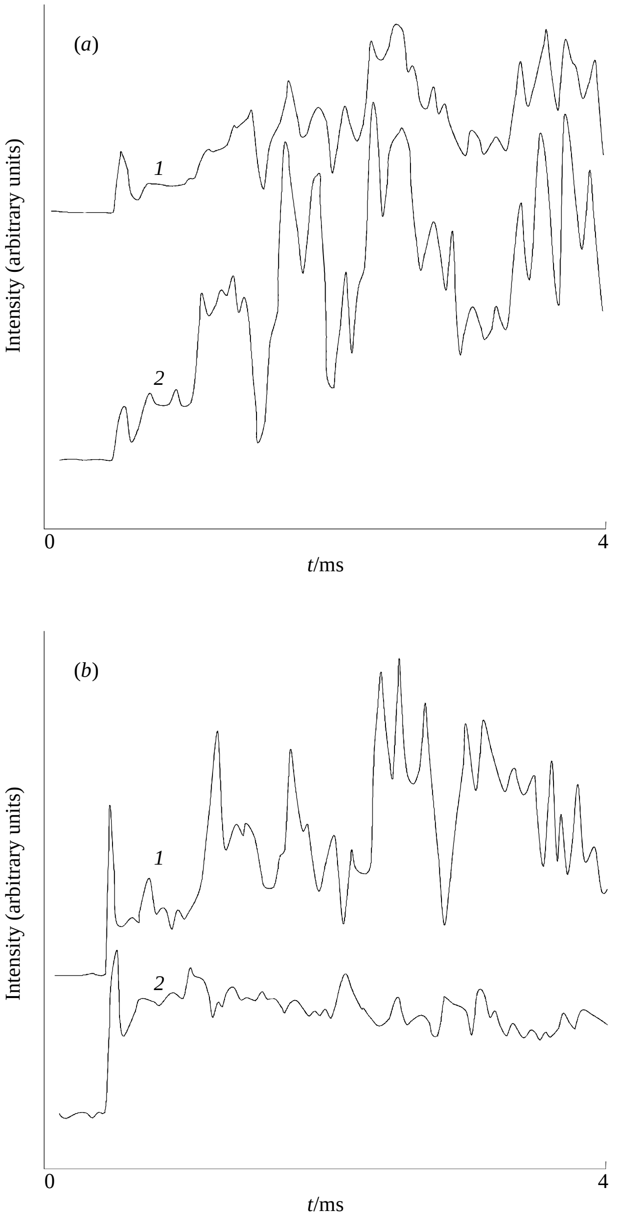

Figure 2 Simultaneously-recorded light pulses. (*a*): *1*, Na 589 nm and *2*, In 451 nm; (*b*): *1*, Na 589 nm and *2*, H 656 nm. Catholyte 1 mM In^{III} and 0.05 mM Na^{I} in 0.4 mM HCl.

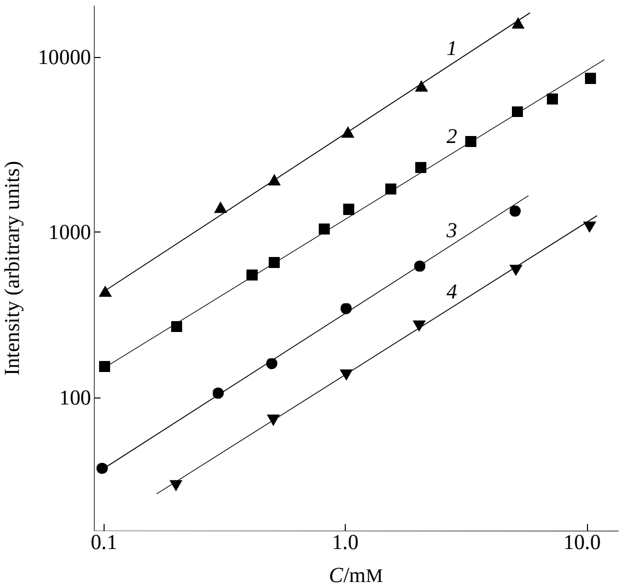

Figure 3 Calibration curves for Na 589 nm (*1* and *3*), K 767 nm (*2*) and Li 671 nm (*4*) lines, with capacity 2 μF (*1, 2* and *4*) and 0.25 μF (*3*).

above-mentioned metal lines it is < 5 eV. Therefore, hydrogen emits only in the thin cathode layer where excitation conditions are very difficult. It is likely that emission of another species with a high excitation potential may be detected if their concentrations are sufficiently great. In contrast, metals may emit in the positive column which is probably many times greater in size than a cathode layer. The oscillations of metal emission intensity appear to be connected with electrolyte sputtering that leads to a synchronism of the kinetic curves of different metals [see Figure 2(*a*)].

The fine structure of the kinetic emission curves is clearly not reproducible but the integrated intensity has a modest relative standard deviation, as seen from Table 1. The flow rate and its pulses, breakdown and sputtering instabilities affect the intensity deviations. To minimize these influences it is reasonable to use internal standardization. The most convenient way is to use the hydrogen line, since it is a constant part of the DSD spectrum independent of the content of dissolved salts. Unfortunately the difference between the nature of the metal and hydrogen emission reduces the usefulness of such a standardization. As shown in Table 1, s_r does not reduce in this case. A greater effect can be achieved by the use of indium as an internal standard. Table 1 indicates that in this case the relative standard deviation s_r does not exceed 0.02.

The dependence of integrated intensity on metal concentration for alkaline metals is not linear. As seen from Figure 3, the curves may be straightened in a log-log scale in the concentration range from 10^{-4} to 10^{-2} M. The gradient is *ca.* 0.8 in all instances. That the gradient is less than one may be related to reabsorption.

Since the electrostatic energy of the condenser is $CU^2/2$, where C and U are capacity and voltage, respectively, a simple calculation shows that in the case of 10 s intermittence time, $C = 2$ μF and $U = 1000$ V, power consumption does not exceed 0.1 W. The estimation is suitable for the DSD source described here with a certain margin (we use $U = 800$ V). The source can be used for alkaline metal determination, with current detection limits 10^{-4} M for Li, 2×10^{-5} M for K and 5×10^{-7} M for Na. It is possible to reduce the capacity and consequently the power consumption by one order of magnitude, at least for the very intense D-line of sodium. As illustrated in Figure 3, calibration plots for sodium with $C = 2$ μF (curve *1*) and $C = 0.25$ μF (curve *3*) differ only by the shift along the vertical axis. A DSD source with $C = 0.25$ μF and power consumption of *ca.* 0.01 W may be used for sodium determination with a detection limit of 10^{-5} M.

Reasonable reproducibility and low power consumption allow us to hope that DSD may be used as a source in AES sensors. The source is not bright and obviously it is not appropriate for trace analysis. One possible application of DSD lies in the monitoring of Na, K, Mg and Ca, which are the major metal components of water in most cases. There are some features of DSD which make it more appropriate for sensors than other kinds of discharges with electrolyte surfaces. Firstly, the absence of solid/plasma interfaces enables the memory effect to be avoided, which is usually caused by erosion and contamination of electrodes. Secondly, the breakdown apparently provides more effective electrolyte sputtering than in the case of continuous discharges.

References

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