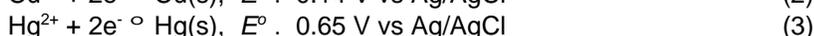
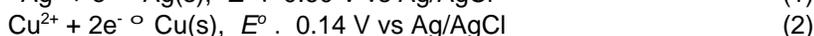
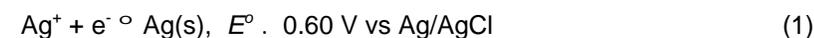


# Electrolytic Deposition of Metals onto the High Voltage Contact in an ES Emitter

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Electrolytic reactions in the ES emitter sustain the production of charged droplets and gas-phase ions by the ES ion source. It is shown here that  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  ions in solution can be electrolytically reduced and deposited as the respective metals onto the surface of the high voltage contact in the ES emitter in negative ion mode. The deposited metals may be liberated from the surface back into solution, by switching the ES high voltage polarity to operate in the positive ion mode, where they are detected in the ES mass spectrum (eqs 1, 2, and 3)



Analytical standards of the respective metals were prepared in  $\text{H}_2\text{O}$  containing 0.75% (v/v) HOAc. ES-MS experiments were performed on a PE SCIEX API165 single quadrupole using a modified TurbolonSpray™ source (Figure 1) with a flow rate of 20  $\mu\text{L}/\text{min}$ . Interface conditions maximized signal for the bare metal ions in positive ion mode;  $^{107}\text{Ag}^+$  and  $^{109}\text{Ag}^+$  at  $m/z$  107 and 109 (0.5 s dwell time each),  $^{65}\text{Cu}^+$  at  $m/z$  65 (1.0 s dwell time), and  $^{202}\text{Hg}^+$  at  $m/z$  202 (1.0 s dwell time). The instrument was programmed to record the ion

signals at the respective  $m/z$  values in both positive and negative ion mode while switching between positive ion mode (10 min), negative ion mode (25 min), and positive ion mode (15 min) during the course of one experiment. A sample was injected at 7.5 min into the first positive ion mode section of the experiment. The injection was stopped after 10 minutes into the negative ion mode portion of the experiment (10.5 min injection).

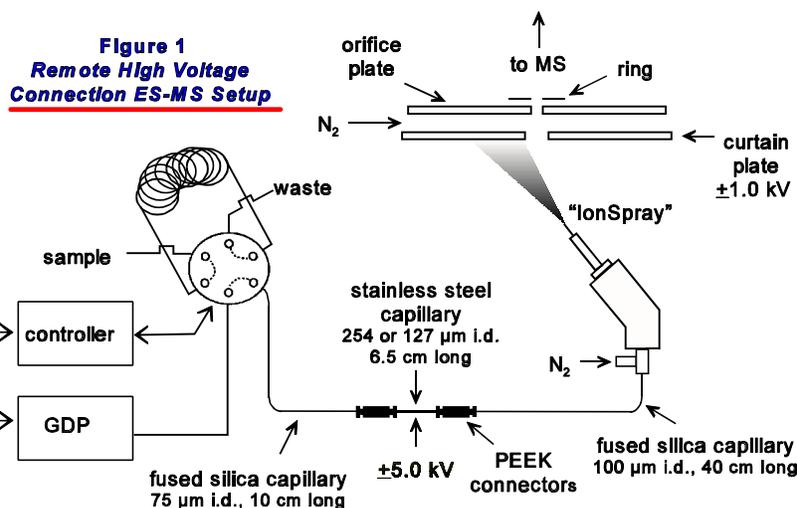
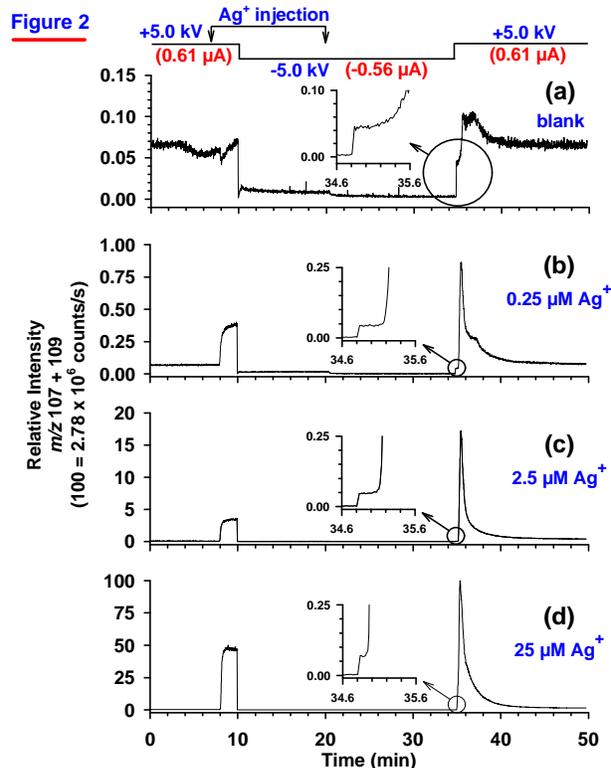


Figure 2 shows the summed ion current profiles in four separate experiments in which (a) a sample blank, (b) 0.25, (c) 2.5, and (d) 25  $\mu\text{M}$   $\text{Ag}^+$  were injected into the ES-MS setup shown in Figure 1. The timing sequence above the panels shows the high voltage applied to the upstream stainless steel capillary (254  $\mu\text{m}$ -i.d.) and the time window of  $\text{Ag}^+$  injection. The  $i_{ES}$  measured during each of the 3 segments of the experiments is also shown. Ion current profiles are normalized relative to the largest signal in panel (d). The observation of "delayed"  $\text{Ag}^+$  stripping peaks confirms that  $\text{Ag}$  is deposited on the upstream high voltage contact in the ES emitter during the negative ion mode of operation. This deposit is oxidized when the ES high voltage polarity is switched for operation in positive ion mode. Oxidation of the  $\text{Ag}$  deposit releases (strips)  $\text{Ag}^+$  back into solution where it flows downstream and is detected by the mass spectrometer as it exits the fused silica spray capillary.

A semi-quantitative analysis of these data reveals that the plateau signals for the three sample injections

increase in rough proportion to the concentration of  $\text{Ag}^+$  in the solution injected. The height and area of the  $\text{Ag}^+$  stripping peaks also increase with the increasing concentration of the  $\text{Ag}^+$  injected. However, the percent recovery, that is, the fraction of the total  $\text{Ag}^+$  injected that deposits, shows no simple correlation with concentration. The fraction of the total ES current,  $i_{ES}$ , in negative ion mode that it is possible to supply via  $\text{Ag}^+$  reduction is calculated as 1.4, 14, and 140% for the injection of 0.25, 25, and 25  $\mu\text{M}$   $\text{Ag}^+$ , respectively. These numbers imply for 25  $\mu\text{M}$  sample that at least 40% of the  $\text{Ag}^+$  would pass through the system unaffected by the electrolysis, because more than enough is present to supply all the necessary current. That might account for the drop in percent recovery for the 25  $\mu\text{M}$  sample injection (25%) compared to the other two experiments. However, these calculations assume that (1) all the  $\text{Ag}^+$  passing through the stainless steel capillary in negative ion mode contacts the metal capillary surface and (2) the potential is sufficient for electrolytic deposition onto the emitter. One or both assumptions do not hold because the percent recoveries are found to be only 33 and 49%, respectively, for the injection of 0.25 and 2.5  $\mu\text{M}$   $\text{Ag}^+$ , not 100%. In any case, *the fraction of  $\text{Ag}^+$  deposited, ranged from 25 to 50% of the total  $\text{Ag}^+$  in the original solution injected. Thus, the concentration of the  $\text{Ag}^+$  exiting the emitter in negative ion mode was significantly decreased relative to the concentration in the original solution entering the emitter. However, the fraction of the total  $\text{Ag}^+$  transported through the system that deposited was not a linear function of the injected  $\text{Ag}^+$  concentration.*



$\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  may also be deposited electrolytically onto the surface of the high voltage contact in the ES emitter (results not shown). To observe a significant stripping peak required a minimum injected concentration of the  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  that was higher than for identical experiments employing  $\text{Ag}^+$  (i.e.,  $\geq 1.5 \mu\text{M}$  for  $\text{Cu}^{2+}$  and  $\geq 25 \mu\text{M}$  for  $\text{Hg}^{2+}$ ). The exact reasons for this are not clear. Of course, in the case of both  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , only half the amount of metal could theoretically be deposited compared to  $\text{Ag}^+$  under identical conditions (i.e.,  $2e^-$  vs  $1e^-$  reactions). Also,  $\text{Cu}^{2+}$  (eq 2) is substantially harder to reduce than  $\text{Ag}^+$  (eq 1), and therefore, the efficiency of this reduction reaction may be less (i.e., other reactions may occur preferentially). In the case of  $\text{Hg}^{2+}$ , which is very easy to reduce (eq 3), the limited stability of a Hg film in contact with a flow stream might restrict the ability to deposit this metal.

The electrochemical nature of the ES ion source could have repercussions for metal determinations and metal speciation studies attempted by ES-MS.  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  and other metals that can be electrolytically reduced within a reasonable potential range may be deposited as a metallic film onto the inner surface of the high voltage contact to the solution in the ES emitter during negative ion mode. The valence state of metals might also be altered by the electrochemical processes in the ES emitter. Thus, ES electrochemistry might be expected to alter in some cases either the intensity or identity of the gas-phase metal ions eventually detected in ES-MS.

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