TECHNICAL NOTE

CRIMINALISTICS

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Effect of Chloride Ion Concentration on the Galvanic Corrosion of α Phase Brass by Eccrine Sweat

ABSTRACT: Inductively coupled plasma mass spectrometry measurement of the relative concentration of sodium, chloride, calcium, and potassium ions in eccrine sweat deposits from 40 donors revealed positive correlations between chloride and sodium ($\rho = 0.684$, $p < 0.01$) and chloride and calcium ions ($\rho = 0.91$, $p < 0.01$). Correlations between ion concentration and the corrosion of α phase brass by the donated sweat were investigated by visual grading of the degree of corrosion, by measuring the copper/zinc ratio using energy-dispersive X-ray spectroscopy, and from a measurement of the potential difference between corroded and uncorroded brass when a large potential was applied to the uncorroded brass. An increasing copper/zinc ratio (indicative of dezincification) was found to correlate positively to both chloride ion concentration and visual grading of corrosion, while visual grading gave correlations with potential difference measurements that were indicative of the preferential surface oxidation of zinc rather than copper.

KEYWORDS: forensic science, latent fingerprint, print visualization, metal corrosion, chloride ion, inductively coupled plasma

The ability of fingerprint sweat to corrode certain metals has been known for nearly one hundred years (1) and has been described historically in relation to workers in the metal industry whose sweat secretions readily corroded metal (and who were known as "rusters") (1,2). It was shown by Collins (1) that the degree of corrosion on metal, measured gravimetrically, was directly proportional to the sodium chloride concentration of artificial sweat placed on the metal. Subsequently, Buckley and Lewis (2) measured chromatographically the chloride ion concentration in eccrine sweat and found that a concentration >0.15 mol readily corroded mild steel. Buckley and Lewis (2) suggested that the measurement of chloride ion concentration in eccrine sweat could be used to identify "rusters" in the metal industry. From an examination of "ruster" patients, Burton et al. (3) were able to confirm earlier results that corrosion of iron and steel was related to sodium chloride concentration in eccrine sweat. Burton et al. (3) proposed a model for this corrosion based on sweat in contact with the metal forming an electrochemical cell with, in the case of iron, oxidation of iron at the anode and hydroxyl ion formation from water and dissolved oxygen at the cathode. The resulting ferrous hydroxide was oxidized rapidly by dissolved oxygen to form brown rust (Fe_2O_3). This model was adapted from one proposed by Evans (4) some years earlier to explain the corrosive action of a differential aeration cell.

While today the quantification of sodium chloride or chloride ion concentration in eccrine sweat is used routinely for the early detection of medical conditions such as pancreatitis (5) or cystic fibrosis (6), it is only recently that sodium chloride concentration (7–10) or chloride ion concentration (11) has been suggested as a factor in determining the visualization of fingerprint sweat corrosion of metals. To date, these suggestions have been qualitative, based on observations of the varying degree of corrosion to metals such as iron and brass caused by different people donating fingerprints.

Previous work on the corrosion of α phase brass in the presence of chloride ions has shown both zinc and copper to be involved in the corrosion process via the formation of complex metal chloride ions (12), a more involved process than that suggested by Evans (4). In this scenario, surface copper can undergo the following reaction.

$$Cu + Cl^- \rightarrow CuCl_{ads} + e^- \qquad (1)$$
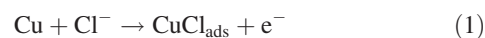
where ads represents adsorbed and implies the reaction occurs in the solid phase at the brass/fingerprint sweat interface. Further reaction with chloride ions can form the complex

$$CuCl_{ads} + Cl^- \rightarrow CuCl_2^- \qquad (2)$$

which can undergo hydrolysis to form a copper (I) oxide corrosion product and, importantly, hydrogen ions, which reduces the pH and accelerates the corrosion process (13)

$$2CuCl_2^- + H_2O \rightarrow Cu_2O + 2H^+ + 4Cl^- \qquad (3)$$

Similarly, chloride ions can react with surface zinc to form a zinc complex

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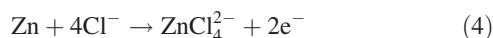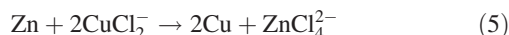
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$$Zn + 4Cl^- \rightarrow ZnCl_4^{2-} + 2e^- \qquad (4)$$

or with the complex $CuCl_2^-$ to give

$$Zn + 2CuCl_2^- \rightarrow 2Cu + ZnCl_4^{2-} \qquad (5)$$

Again, this zinc complex can undergo hydrolysis to form a zinc oxide corrosion product and hydrogen ions

$$ZnCl_4^{2-} + H_2O \rightarrow ZnO + 2H^+ + 4Cl^- \qquad (6)$$
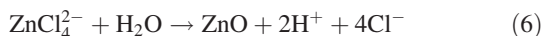
In both Eqs (3) and (6), formation of the metal oxide results not only in a lowering of the pH (through the production of hydrogen ions), but also the release of chloride ions back into solution, which can then continue the metal oxidation process. This mechanism is more complex than that proposed previously for eccrine sweat corrosion of brass (14), which was based on Evans' model (4).

In this technical note, we measure the relative concentration of ions found commonly in eccrine sweat (15) by means of inductively coupled plasma mass spectrometry (ICP-MS) and correlate this to the age and gender of the fingerprint donors. We then correlate ion concentration to eccrine fingerprint sweat corrosion of α phase brass. Fingerprint sweat corrosion is measured by three separate means. First, by a visual determination of the fingerprint ridge pattern corrosion on the brass (10), second by measuring the copper/zinc ratio of the brass (and hence dezincification at a depth of up to ~2 μm) using energy-dispersive X-ray spectroscopy (EDX), and last by measuring the potential difference (ΔV) between corroded and uncorroded metal when a large potential (V) of ±1400 V is applied to the uncorroded metal (10,16,17).

Experimental Details

Materials and Method

For these experiments, 20 men and 20 women donors were selected, with five donors of each gender in each of the age ranges 21–30, 31–40, 41–50, and 51+ years. Each donor deposited fingerprint sweat from one finger onto 1 mm thick 25 mm diameter α phase brass disks (68Cu-32Zn by percentage weight) (10,16,17). Fingerprint sweat from the remaining nine fingers of each donor was collected by each donor placing each of the nine fingers in turn onto a glass microscope slide through a polyethylene terephthalate (PET) template. The PET template ensured a uniform sweat collection area between donors. Before deposition, each donor rubbed their hands together to ensure a uniform distribution of eccrine sweat as previous research has indicated that chloride ion concentration can differ between fingers for the same individual (15). Prior to use, each microscope slide was rinsed in ultra-pure water and then oven dried for 1 h at 100°C, and each PET template cleaned using a methanol-soaked tissue. Each donor had their own microscope slide and PET template to avoid cross contamination of samples (18).

All brass disks were left in air at room temperature (18 ± 5°C) for a period of 5 days, this time period being in keeping with previous work (10). After the 5-day period, samples were washed in a 0.5 L solution of warm water containing a few drops of a commercial detergent, the disks being rubbed vigorously with a nonabrasive cloth to remove all traces of fingerprint deposit. This washing regime has been shown to effectively remove the fingerprint deposit (but not the corrosion) from the surface of brass disks (19).

ICP-MS samples were prepared by placing the glass slide from a donor into a 600-mL glass beaker and adding 7.5 mL of ultra-pure water. The beaker was then sonicated for 10 min and the washings analyzed with ICP-MS. Prior to use, the glass beakers were cleaned in a base bath overnight and then rinsed in an acid bath before being rinsed in de-ionized water followed by acetone. Beakers were then oven dried for 1 h at 100°C and left to cool overnight (18). A separate beaker was used for each donor to avoid cross contamination. This collection and cleaning regime was based on previously identified good practice for collecting and processing small volumes of fingerprint sweat (18).

ICP-MS spectra were recorded with an Agilent 7500ce instrument (Agilent Technologies, Oxford, UK) operating with a radiofrequency power of 1500 W, an Argon carrier gas flow rate of 0.8 L/min, an Argon makeup gas flow rate of 0.25 L/min, and a spray chamber temperature of 2°C.

EDX was carried out with a JSM 820M instrument by Jeol (Welwyn Garden City, UK) and operated at 8 kV for imaging samples and 18 or 28 kV for EDX elemental analysis. The EDX spectrometer was an Oxford Link Isis instrument (Oxford Instruments, Abingdon, UK) with a Beryllium window and cooled by liquid nitrogen. The higher potential (28 kV) was used for elemental analysis to increase the depth of field.

Results and Discussion

Ion Concentrations

A comparison of the relative concentration of sodium, chloride, calcium, and potassium ions from ICP-MS showed a statistically significant positive correlation between chloride and sodium ions ($\rho = 0.684$, $p < 0.01$) and chloride and calcium ions ($\rho = 0.91$, $p < 0.01$), with a two-tailed Spearman's correlation (20). Figure 1 shows sodium and calcium concentrations plotted against chloride ion concentration for concentrations >0.01 ppm together with a least squares regression in which $R^2 = 0.17$ for sodium and chloride and $R^2 = 0.85$ for calcium and chloride. In addition to the much better correlation between calcium and chloride ions compared with sodium and chloride ions, there was a positive correlation between the concentrations of all four ions. This is not surprising and is indicative of a greater quantity of sweat deposit containing a greater amount of substance. The greater concentration of calcium (compared with sodium) is more surprising as previous results suggest that, generally, eccrine sweat contains a greater amount of sodium (0.03–0.25 mol) than calcium (0.007 mol) (15). Clearly, other ions present (and not measured here) may affect the concentrations deposited by an individual, with both bicarbonate and
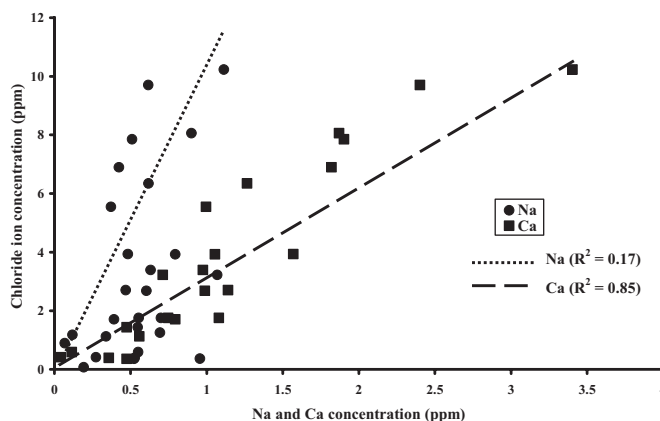

FIG. 1—*Chloride ion concentration plotted against sodium ion and calcium ion concentrations for concentrations >0.01 ppm.*

ammonia having concentrations of the same order as those measured here (15). Also, the ubiquitous nature of sodium means that measured concentrations could have been affected by contamination. However, there was no evidence for this, and for each ICP-MS analysis, a blank solution of ultra-pure water from a glass slide extraction was first analyzed. This was to ensure that there was no contamination of ions arising from washing the microscope slides.

Age and Gender of Donors

Figures 2 and 3 show the relative mean concentration of the four measured ions compared to the age range and gender, respectively, of the 40 donors. From Fig. 2, the chloride ion concentration can be seen to be much greater for donors in the group aged 21–30 than for all other age groups (aged 31+), and from Fig. 3, the chloride ion concentration for male donors is much greater than for female donors. In both cases, this difference was found to be statistically significant with $p < 0.01$ using a two-tailed Mann–Whitney test (20). For age range, the Mann–Whitney test compared the 21–30 age group with all the other age groups taken together. Clearly, the notion that persons in the age group 21–30 had a greater chloride ion concentration than older groups was observed experimentally, rather than being formed in advance. Therefore, the statistical
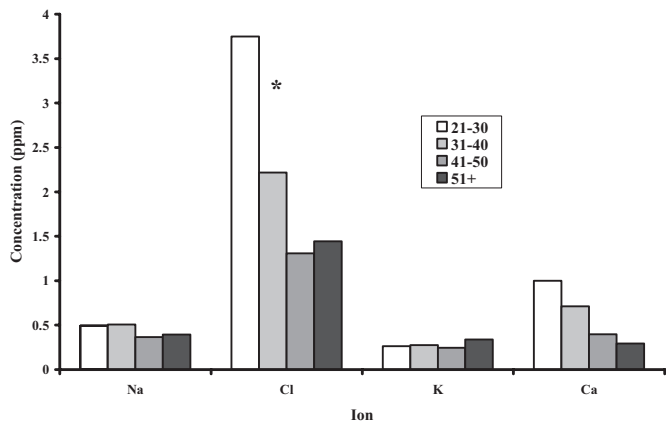
validity of this as an hypothesis would require testing on a different data set. While it has been well established that the chemical content of sebum varies with age, it is likely that other factors such as diet and lifestyle would have affected the results shown here (http://www.thetechherald.com/article.php/200838/2037/Sweaty-criminals-with-bad-diets-prone-to-new-forensic-technology [accessed April 13, 2011]).

Ion Concentration and Visual Grading of Corrosion

Eccrine sweat corrosion of the brass disks from each of the 40 donors was graded based on the quality of ridge detail visible (as corrosion) after washing the disks as described above. For this, the grading system devised by Bandey (21) was used and this is reproduced in Table 1. A statistically significant positive correlation was measured between this grading and sodium ($\rho = 0.333$, $p < 0.05$), calcium ($\rho = 0.287$, $p < 0.05$), and potassium ($\rho = 0.282$, $p < 0.05$) ion concentrations with a two-tailed Spearman's correlation (20). It will be noted that the magnitude of ρ is less than that observed above for the correlation between ions and also the degree of confidence is lower ($p < 0.05$). Perhaps surprisingly, no statistically significant correlation was measured for the chloride ion concentration and visual grading. This relatively poorer correlation may be due to the grading system, which is based on a visual measure and also there being only five distinct grading bands, making some disks difficult to grade accurately.

Ion Concentration and EDX

EDX analysis was performed on disks from 10 of the 40 donors where there was clear visible fingerprint corrosion of the brass, as described above. From EDX, the copper/zinc ratio at a depth of up to ~2 μm was calculated and gave a statistically significant positive correlation to the measured chloride ion concentration for these 10 donors ($\rho = 0.523$, $p < 0.05$) with a two-tailed Spearman's correlation (20). Figure 4 shows the copper/zinc ratio plotted

FIG. 2—*Sodium, chloride, potassium, and calcium ion concentrations plotted against age of donor. The asterisk indicates the chloride ion concentration to be statistically significant for the 21–30 age group* (p < 0.01).
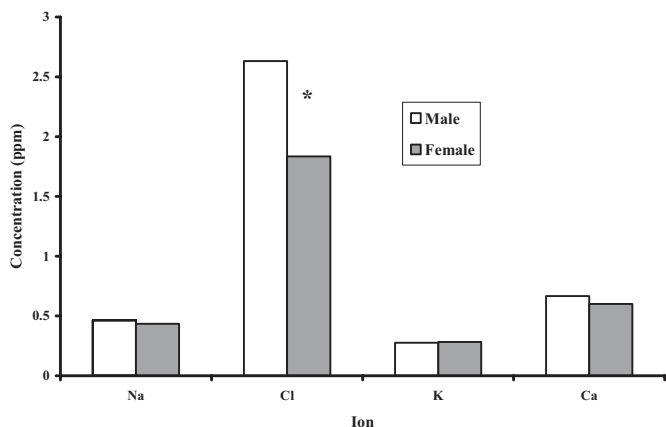
FIG. 3—*Sodium, chloride, potassium, and calcium ion concentrations plotted against gender of donor. The asterisk indicates the difference in chloride ion concentration between males and females to be statistically significant* (p < 0.01).

TABLE 1—*Grading system for determining the quality of ridge detail for fingerprint corrosion of brass disks devised by Bandey (21).*

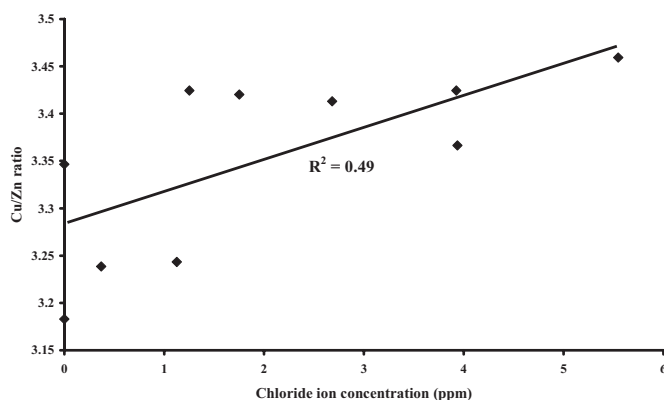| Grade	Comments
0	No development
1	No continuous ridges. All discontinuous or dotty
2	One-third of mark continuous ridges. (Rest no development, dotty)
3	Two-thirds of mark continuous ridges. (Rest no development, dotty)
4	Full development. Whole mark continuous ridges

FIG. 4—*Copper/zinc ratio plotted against chloride ion concentration.*

against chloride ion concentration, together with a least squares regression in which $R^2 = 0.49$. Again, for these 10 donors, there was a statistically significant correlation between the chloride ion concentration and the calcium ion concentration ($\rho = 0.87$, $p < 0.01$).

An increasing copper/zinc ratio is indicative of dezincification of the brass, which is well known to corrosion science to be accelerated with increased chloride ion concentration (13). These results are consistent therefore with earlier work described above that showed a correlation between sodium chloride or chloride ion concentration in eccrine sweat and visible corrosion of metal (1–3).

Although the visible grading of corrosion did not give a statistically significant correlation with chloride ion concentration (whereas the copper/zinc ratio did), visible grading did give a statistically significant positive correlation to the copper/zinc ratio ($\rho = 0.565$, $p < 0.05$) with a two-tailed Spearman's correlation (20).

Ion Concentration and ΔV

Dezincification of brass from eccrine sweat as observed above has been shown previously to enable the resulting fingerprint corrosion to be enhanced by the application of a large potential (V) to the uncorroded metal (10). The potential difference arising between corroded and uncorroded metal (ΔV) enables a conducting powder to adhere preferentially to areas of corrosion (and thereby enhance the visualization of the fingerprint) provided ΔV is of sufficient magnitude. The magnitude of ΔV has been shown to be dependent on the copper/zinc ratio at the surface of the brass (16,17).

ΔV was measured for disks from 17 of the 40 donors. These 17 included the 10 referred to in the previous section with additional disks where the corrosion was less visible. For $V = \pm 1400V$, ΔV was measured using apparatus described previously (16,17). This apparatus enabled electrical contact to be made with corroded areas of the disk by means of a platinum or copper rod ~ 0.5 mm diameter, formed into a tip at one end ~ 55 μm diameter. This tip diameter was larger than that used previously (16) as the larger diameter was found to give more reproducible results (17). For each disk and polarity of V ($\pm 1400V$), ΔV was measured at several points and averaged using both the platinum and copper probes. Like the visible grading, no statistically significant correlation could be found between ΔV and chloride ion concentration. However, a statistically significant correlation was found between ΔV and the visible grading for both positive V ($\rho = -0.452$, $p < 0.05$) and negative V ($\rho = 0.506$, $p < 0.05$) with the copper probe.
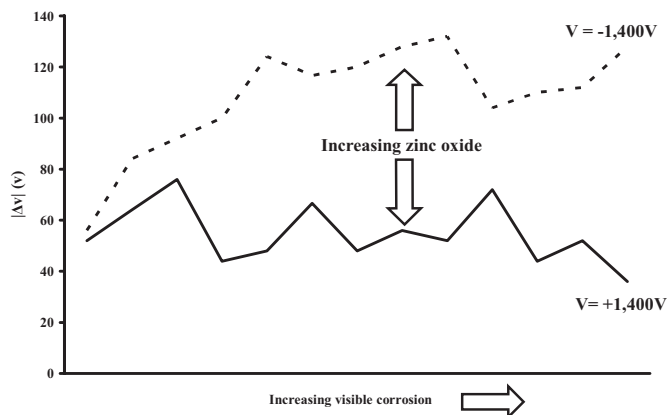
Interestingly, it can be seen that a positive V had a negative correlation with visible grading, while a negative V had a positive correlation. Thus, as the visibility of the corrosion increased ΔV for a positive V decreased and vice versa for a negative V. A decreasing ΔV for positive V and increasing ΔV for negative V has been shown previously to be indicative of an increase in zinc corrosion products (typically zinc oxide) coupled with a decrease in copper corrosion products (typically copper (I) oxide) (16,17). Thus, an increase in visible grading (i.e., a more developed pattern of fingerprint ridge corrosion) is consistent with oxidation of zinc rather than copper. This is illustrated in Fig. 5, which shows a plot of $|\Delta V|$ against visible grading for the 17 disks examined.

$|\Delta V|$ did not give a statistically significant correlation to the copper/zinc ratio.

Conclusion

From an ICP-MS analysis of the relative concentrations of four elements found commonly in eccrine sweat (sodium, chlorine, calcium, and potassium) from 40 donors, correlations have been derived between these concentrations and the corrosion of α phase brass. Corrosion has been determined by a visible grading, by EDX and by a potential difference (ΔV) measurement. The EDX copper/zinc ratio has been shown to correlate positively to both the chloride ion concentration and visible grading, while the visible grading gave correlations with ΔV that were consistent with preferential surface oxidation of zinc rather than copper. From this, it might have been anticipated that ΔV would have given a statistically significant correlation with chloride ion concentration but this was not observed. Further, the EDX copper/zinc ratio suggests increasing removal of zinc (dezincification) as both chloride ion concentration and visible grading of corrosion increase, whereas the correlation between visible grading and ΔV suggests greater surface oxidation of zinc as visible grading increases. This apparent dichotomy may be explained as the EDX measurements are at a depth of up to ~ 2 μm below the surface, whereas the measurements of ΔV are made at the surface. This could be investigated further by more quantitative measures of the chemical and electronic state of the corrosion, as EDX gives no information about the oxidation state of elements. Measurement of the pH of the donated sweat would also be useful as previous work suggests eccrine sweat has, generally, pH < 7.0 (15), and a low pH, particularly in the presence of chloride ions, is known to accelerate corrosion (13).

As visible grading is based on the number of complete ridges observed as corrosion, the use of these more quantitative measures are likely to give further insight into the relationship between chloride ion concentration in eccrine sweat and the visualization of fingerprint corrosion of brass.

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FIG. 5—*ΔV (measured with the copper probe), shown plotted against visible corrosion of brass disks.*

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