PRELIMINARY STUDIES OF METALLIC BONDING BETWEEN LIQUID MERCURY AND TRACE CONTAMINANTS USING A NEW SAMPLING TECHNIQUE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • NOVEMBER 1971
A technique of microsampling a metal surface at a single "point" that combines principles of electrostatics, electrochemistry, ion exchange and emission spectrographic analysis is described. The method can be used to perform chemical analysis or to provide information about the nature of metallic bonding and kinetic processes at electrode surfaces. It has been used to study trace element contamination in liquid mercury. Results indicate the formation of compounds with mercury whose properties change with time and whose composition may be influenced both by the method used to add the contaminant and by the presence of contamination other than that being studied.
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Preliminary Studies of Metallic Bonding Between Liquid Mercury and Trace Contaminants Using a New Sampling Technique*

by Ronald Razner

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Summary

A method of microsampling a metal surface at a single "point" has been developed which can detect elements present in trace amounts, and is adaptable to the study of metallic bonding and kinetic processes occurring at electrode surfaces. The method is based on a combination of principles from electrostatics, electrochemistry, ion exchange, and emission spectrographic analysis. It was used to study trace-element contamination in liquid mercury, where compound formations and surface concentration can occur. Results of experiments where specific contaminants were added to mercury indicate the formation of compounds whose properties change with time and whose composition may be influenced both by the method used to add the contaminant, and by the presence of contamination other than that being studied. Oxidation reactions at mercury electrode surfaces show similar variability. In particular, some evidence suggests that the oxidation of mercury itself may require the presence of at least trace amounts of contamination. Implications of these results for various scientific and engineering uses of mercury are discussed. Possible applications of the microsampling technique as a research tool in metallurgical and electrochemical research are also considered.

Introduction

Material contained in this report is taken from heretofore unpublished results in the author's master's thesis (ref. 1), which represent the outcome of a research project directed at developing techniques for the trace-element analysis of liquid mercury. The problem had its origin in the fact that small concentrations of contaminant can

*Part of the material presented in this report was submitted as a thesis in partial fulfillment of the requirements for the degree Master of Science, University of Wisconsin, June 1961.
influence the surface tension and other properties of liquid metals (ref. 2, p. 494). In addition, theoretical attempts to understand the principles governing surface properties of liquid metals (see refs. 3 and 4 for reviews) have not been particularly successful (ref. 2, p. 490). This lack of adequate understanding presents problems for many areas of research and development, such as the use of liquid metals in heat exchange circuits, and uses of mercury in electronic switching circuits, ion propulsion engines and electrochemical analysis. Consequently, a preliminary problem involves the developing of methods for the qualitative and quantitative analysis for trace elements, inasmuch as the existence of adequate methods of chemical analysis must necessarily precede the detailed study of effects.

The author's work on the trace-element analysis of mercury started as part of an undergraduate thesis (ref. 5) where the possibilities of emission spectrographic analysis were evaluated. Various approaches of ion exchange separation were studied using analogies to methods of rare earth separation developed during the Manhattan Project. In this preliminary work all extraction of mercury aliquots from a bulk sample for analysis was done with the assumption that the bulk sample would be of uniform composition if only traces of foreign metals (total contamination less than 0.1 percent by weight) were present. That assumption was later found to be faulty, even at much lower levels of contamination. From this and other extensive work on the spectrographic approach (ref. 6, p. 43), it appears that lower detectability limits of the order of $10^{-4}$, $10^{-8}$, and $10^{-7}$ percent by weight of Copper, Magnesium, or Calcium, respectively, might be achieved without concentrating the impurities, with perhaps higher limits for the majority of other metals. However, this was considered unacceptable because levels of contamination in the order of $10^{-4}$ to $10^{-5}$ percent by weight of any contaminant represented the desired starting point.

Methods of ion exchange separation using the best available reagent-grade chemicals and resins were also found to be unworkable, in that the reagents themselves contributed levels of contamination much greater than that being sought. As a result, attempts were made to prepare all necessary materials in spectrographically pure form, meaning that levels of contamination were beyond spectrographic limits of detectability. The ion exchange resins, when finally purified, presented a new problem in that contaminants being sought were too strongly adsorbed onto the resin material to be effectively recovered from an ion exchange column by elution. In fact, it was a common experience that species supposedly existing as cations would be quite strongly taken up by an anion exchanger, and vice versa (at trace levels). As a result of these problems, a method of analysis was sought that would combine the most desirable features of emission spectrographic analysis and the properties of ion exchange resins, while taking into account suspected sampling requirements for liquid mercury as outlined below.
Related to the fact that trace-element contamination in liquid mercury influences its surface tension, considerable research has been done that attempts to correlate properties of mercury with surface-tension measurements. If successful, such measurements might themselves provide an indicator of trace-element contamination. However, surface tension measurements have not led to any definite conclusions about the structure of liquid metals and alloys (ref. 2, p. 496). To be applicable to a bulk sample of mercury, any chemical analysis based on surface tension measurements would in addition have to assume a homogeneous sample if the data are to have any meaning consistent with present sampling techniques. (A recent detailed review of known techniques for the sampling and analysis of metals and alloys - other than that to be presented herein - is given in ref. 7.) As work on this project progressed (refs. 1 and 5) it became evident that the assumption of homogeneity is probably far from the truth. It appeared that there were definite cases where a surface concentration of contaminants occurs, and still other cases where this does not happen. Moreover, in preparing amalgam standards for analytical work, it was difficult to obtain reproducible results. This problem appeared to reflect experiences often encountered by other workers, where information regarding liquid-metal alloys is not always reliable, and sometimes contradictory (ref. 2, p. 494).

After some consideration, it became evident that one could perhaps obtain several different types of compound formations (collectively referred to in this report as "bound states") of metals with mercury. This in itself is not surprising since many compound formations in liquid metal systems are known (see, e.g., ref. 2, table XXVIII) that, in fact, do not conform to a clear-cut law of definite proportions (ref. 8, p. 394). However, results seemed to point to the possibility that compound formation depends on the source of the metal contaminant, that is, whether an amalgam was prepared by dissolving a neutral metal in mercury, or by electrolysis from a salt, and so on. Furthermore, evidence seemed to point to the fact that whatever bound states were being obtained were changing with time and also that some of these would tend to concentrate at the surface, while others would not.

These circumstances make the problem of a trace element analysis for mercury much different from what it would be were one to assume a homogeneous sample. Given an arbitrary volume of mercury, it now becomes necessary to devise a method for a local analysis of the sample. Such method must be sensitive to traces of metal impurities; it must be able to distinguish between different bound states; and it must be localized in order to detect any surface concentration that might occur. In regard to surface concentration, the implications are clear. If a trace impurity in mercury were to concentrate at the surface and form a thin surface film, it not only becomes necessary to detect the presence of this film, but to obtain some insight into its chemical composition. Furthermore, since the amounts of contaminant involved would be very small, a film
resulting from surface concentration may well be of a thickness that would practically eliminate any sampling technique involving a scraping of the surface. Thus, a sampling procedure not only must be capable of obtaining the previously mentioned information, but must disturb any surface film as little as possible. This requirement is necessary because, if a surface film were to be remixed with the underlying sample, any hope of composition analysis would be destroyed.

An approach to this problem was accomplished by applying some well known results of electrostatics to an ion exchange bead, and coupling these with the electrochemical concept of anodic stripping. The resulting method, in addition to providing a means for chemical analysis, was adaptable to studies of the nature and structure of metallic bonding, as well as electrochemical kinetics at metal surfaces. The results reported herein are preliminary in several respects, but are sufficient for assessing the value of the microsampling technique as a potential research tool.

**BASIC CONCEPTS AND THEIR ADAPTATION TO THE MICROSAMPLING OF A METAL SURFACE**

**Basic Concepts**

If an electrically conducting sphere of radius $a$ (carrying no net charge) is placed in a uniform electric field of intensity $E_0$ (fig. 1), it is a well-known result of electrostatics that the sphere undergoes a polarization, and that the charge per unit area on its surface ($r = a$) is given by

$$
\sigma = 3\epsilon E_0 \cos \theta
$$

where $\epsilon$ is the permittivity of the medium (ref. 9, pp. 412 to 414 and ref. 10, pp. 48 to 52). ($\epsilon = \kappa \epsilon_0$ where $\kappa$ is the dielectric constant and $\epsilon_0$ is the permittivity of free space.) Thus, if $\theta = 0$, $\sigma = +3\epsilon E_0$, and if $\theta = \pi$, $\sigma = -3\epsilon E_0$, so that the sphere acquires a positive charge on one half of its surface, and a negative charge on the other half. This holds only on the surface of the sphere, and is a result derived by solving Laplace's equation, $\nabla^2 V = 0$, for $r \geq a$. In electrostatics the potential inside a conducting body is always zero; thus at points $r < a$, the electric intensity is $E_r = -\partial V/\partial r = 0$. (All symbols are defined in appendix A. Expressions are in SI units.) Furthermore, the surface charge density is seen to be independent of $\varphi$, because the problem possesses an axis of azimuthal symmetry (ref. 11, pp. 60 to 64).

Now consider a particle of ion exchange material in the form of a spherical bead (fig. 2). Basically, any ion exchange material consists of a cross linked plastic matrix
to which negative charges (for cation exchangers) or positive charges (for anion exchangers) are anchored by chemical bonding. This combination of plastic matrix and anchored charges (of a single polarity) form the immobile part of the ion exchange material. Providing for overall electroneutrality of this arrangement are mobile ions of opposite charge, depicted in figure 2 as a charge cloud surrounding the bead. Thus, one has a direct analogy between a particle of ion exchange material and an ordinary metallic conductor. Whereas the metallic conductor consists of an array of heavy (thus relatively immobile), positively charged atomic nuclei surrounded by highly mobile, loosely bound conduction electrons, the particle of ion exchange material is a plastic array to which charges of one polarity are anchored, while charges of the opposite polarity are free to roam and exchange places with any charges of like polarity that might exist in the surrounding environment.

By combining the analogy of an ion exchange bead as an electric conductor with the conducting sphere problem depicted in figure 1, one has the elements of a sampling technique for a metal surface that can fulfill many, if not all, of the requirements set forth in the preceding section. To this end consider the case where the charge cloud in figure 2 is in the form of hydronium ions ($H_3O^+$, or for simplicity $H^+$), and a spherical bead of this material is placed between capacitor plates in a dielectric medium of water (fig. 3). Just as in figure 1, the ion exchange bead will be polarized due to $H^+$ drift. If one now substitutes a mercury surface for the positive capacitor plate and a
thin wire with coordinates \((r >> a \text{ for all } r, \theta = 0)\) for the negative capacitor plate and if one encloses the system in a cylinder with its axis parallel to the azimuth, he now has the geometrical arrangement shown in figure 4. Even though the electric field is no longer uniform, two essential features of the original conducting sphere problem have been preserved: One is an axis of azimuthal symmetry that makes the charge density on the polarized bead independent of \(\varphi\), and the other is the intuitively evident fact that this charge density has maxima at \(\theta = 0\) and \(\pi\). If one now replaces the water dielectric medium with a slightly leaky dielectric \((10^{-5} \text{ to } 10^{-4} \text{ M HCl in present experiments})\) the arrangement in figure 4 becomes an electrolysis cell where metal species will be anodically stripped from the mercury surface. Furthermore, since the ion exchange bead is a conductor, it will serve as an electric shield between the mercury surface and the primary cathode. The negative charge density on the bead, in effect, acts as a secondary cathode, and since this density is a maximum at \(\theta = \pi\), the effective "applied potential" for the cell can be expected to reach a maximum at the point of closest approach of the bead to the mercury surface. (The positive charge density at the mercury anode will also be a maximum at the point of closest approach for the same reason that the capacitance of a capacitor is inversely proportional to the dielectric thickness.) Consequently, a "local cell" results, where anodic stripping activity can be expected
to be most vigorous around $\theta = \pi$. As metal species are oxidized ($M - ne^- \rightarrow M^{n+}$) positive ions flow onto the surface of the bead. As the process continues, excess $H^+$ ions no longer needed for charge balance at the exchange sites drift up the bead and into solution in the vicinity of $\theta = 0$, while $H_2$ gas is, in turn, evolved at the primary cathode. (As long as the concentration of HCl was not significantly increased beyond that stated, no problem was encountered by oxidation of $Cl^-$ at the anode.) This process assumes that all $M^{n+}$ produced will be held more strongly than $H^+$ at the exchange sites of the bead and also that $H^+$ ions, being the most mobile, will preferentially drift to the top of the bead. Such selectivity of $M^{n+}$ over $H^+$ is easily achieved with many commercial cation exchange resins. Now all that is necessary in order to determine what has been stripped from the mercury surface is to extract the bead from the electrolysis cell and subject it to an emission spectrographic analysis.

Advantages and Possible Uses of the Microsampling Concept

As an analytical microsampling technique, the preceding process has several unique features. First, the bead can get very close to an electrode surface and directly sample species in the vicinity of the metal-solution boundary. If the bead does not actually make physical contact with the surface but is separated from it by a thin aqueous film (see discussion at end of present section), then it is reasonable to assume that the ion exchange bead can sample what comes off the electrode surface without the chemical composition of the bead material entering into the electrochemical kinetics (other than its acting as the secondary cathode). In contrast to many techniques of electrochemical analysis where an electrode surface is exposed to high concentrations of salt solutions (for example, supporting electrolytes in polarographic analysis; ref. 12, pp. 122 to 128) the present technique is capable of operation with little or no contamination of the metal surface from the metal-solution boundary. Consequently, with a sampling technique of this type, one can approach an experimental situation where measurements are indicative of properties of the metal surface itself without complications due to metallic ions in the electrolyte (other than those due to oxidation of the surface). This is a distinct and necessary advantage when influences due to trace elements are being studied. Also the method requires very few spectrographically pure chemicals, which are expensive and difficult to prepare.

Hydrochloric acid was used as the leaky dielectric because it is easy to prepare in spectrographically pure form, and it will not itself attack the mercury surface. The only possible reaction with mercury could be the formation of a minute amount of calomel at the electrode surface (which in turn is only very slightly soluble in water). In the experiments to be presented herein, it will be seen that there were several instances
where no mercury at all showed up on a bead, thus indicating that any reactions due to the trace of Cl⁻ in the dielectric were not extensive enough to cause interferences. Other acids are either extremely difficult to prepare spectrographically pure, or they will not be ionized highly enough for efficient H⁺ transport, or they will react with the mercury surface to form soluble mercury species that would then show up consistently on beads. One should not expect trouble from diffusion of Cl⁻ ions toward the mercury surface from above the bead because such ions must first enter the region θ ≥ π/2 of the polarized bead, where they would tend to be repelled by the increasingly negative field gradient. In effect, the top hemisphere of the bead acts as a secondary anode. But Cl⁻ cannot be oxidized here either because the bead itself is not an electron sink—only a source of H⁺ ions.

One is always at an advantage if he can anticipate possible complications in the study of a physical system and construct his experiments to take these into account. Accordingly, it is appropriate at this point to consider some of the things one might expect to learn from the proposed microsampling technique concerning amalgam formations, and the rate of formation, composition and oxidation properties of surface films. If one were to electroplate a contaminant into a bulk sample of mercury, it would evidently be possible to detect the existence and rate of formation of a surface film by setting up several identical electrolysis cells (less the ion exchange bead) immediately after adding the contaminant, and by performing individual electrolysis experiments at various time intervals. This would be especially appropriate for slowly forming films, where rates might be measured in terms of hours, days, and even longer. Also, some insight as to composition could be obtained from an analysis of the types and relative amounts of species that show up on the beads.

More subtle are questions regarding composition in relation to oxidation properties of amalgams. In the following let (A<>B) designate possible bound state relationship(s) between metallic species A and B. Now consider the electrodeposition of A⁺⁺⁺sol from an aqueous solution of one of its salts into mercury, with formation of (Hg<>A). (Hg<>A<>A), (Hg<>A<>Hg), (Hg<>A), ⋯. (Subscript "sol" indicates a species in aqueous solution.) If this is followed by an attempt to reverse the process, that is, to anodically strip species A back into solution, three possibilities arise for each bound state (where subscript "elect" indicates a species remaining in the electrode):
The side reaction in the third case indicates the possibility of "recycling" at the electrode surface to yield more bound states of the same and/or different structure. In other words, questions arise as to whether the original species (or Hg) or a combination of these is stripped out, as to whether "decomposition potentials" for the various possibilities are nearly the same or distinctly different, and as to the correct interpretation of the electric current involved in the electrolysis.

Carrying these considerations one step further, suppose now that contaminants A and B were added to mercury. Then one would have possibilities for bound state relationships (A → Hg → B), (A → B → Hg), (B → A → Hg), (A → B → Hg), ... Thus, depending on what is formed, it may or may not be possible to anodically strip a given contaminant from the mercury, let alone on a well defined selective basis (that is, when some "decomposition potential" is attained). It is also conceivable that the species electrolyzed out could depend not only on the bound state relations (and their possible changing with time), but on their orientations at the electrode surface. If, for example, species A in a system containing A, B, and Hg could be removed alone at a low voltage, but only B or B and Hg but no A could be removed at a still higher voltage, one might interpret this as the result of a bound state orientation phenomenon at the electrode surface. Some insight and perhaps definitive answers to such general questions might well be obtained with the microsampling concept previously described, especially where only traces of contaminants are present and where one wishes to avoid the complication of mechanical mixing beneath the mercury surface.

Special requirements. - In concluding this section, it is necessary to elaborate on the concept of an ion exchange bead as a conductor; on the possibility that a bead in the proposed cell could make physical contact with the mercury surface; and finally on properties to be considered in selecting a suitable ion exchange resin.

The classification of a substance as a "conductor" is not absolute in the sense that conductor properties in one situation imply conductor properties for any situation. Rather, the time scale of events for a given experiment must be considered, and the material's ability to respond to changing electrical forces in terms of that time scale. For infinite times, the only property needed for a material to be a conductor is the
existence of a mobile component with the ability to respond to an electromotive force in
a finite time. Now consider an arbitrary (ohmic) material of conductivity $g$ and dielec-
tric constant $\kappa$ which has a volume density of free charge $\rho_0(\vec{r})$ in the presence of some
externally applied electromagnetic influence. If this influence is suddenly turned off,
the material in question will tend to approach the equilibrium condition of no excess
interior charge (the static condition being one where free charges exist only on surfaces
or on boundaries between different media). Let $\vec{j}$ be the vector current density. Then,
by the equation of continuity, $\partial \rho / \partial t + \nabla \cdot \vec{j} = 0$, and by Ohm's law, $\vec{j} = g(\vec{E}) \vec{E}$, one has
$\partial \rho / \partial t + g \nabla \cdot \vec{E} = 0$. However, by Maxwell's equations (refs. 9 to 11), $\nabla \cdot \vec{E} = \rho / \epsilon$ for
a linear medium, so that one has the equation $\partial \rho / \partial t + (g / \epsilon) \rho = 0$ with the solution
$\rho(\vec{r}, t) = \rho_0(\vec{r}) \exp (-gt/\epsilon)$. Thus, the equilibrium condition is exponentially approached,
and one sees that the quantity $\epsilon / g$ has the dimensions of time. This is the relaxation
time of the material, and it is a measure of how fast electrostatic equilibrium can be
approached. For the material to be a conductor in a given experimental situation, it is
only necessary that $(\epsilon / g) << 1/\nu$ where $\nu$ is the highest "frequency" encountered. If
in the proposed experiments $1/\nu$ is construed as an electrolysis time (which is of the
order of several minutes to several hours), then a single ion exchange bead can be con-
sidered a conductor if $\text{H}^+$ drift on the bead occurs rapidly enough so that a major por-
tion of the polarization (in response to an applied electromotive force) is completed
before significant electrolysis has a chance to occur. With the present experiments, no
problem was ever encountered in this respect.

The condition that the bead not make actual physical contact with the mercury sur-
face is desirable for two reasons. First, only in this way can a sampling be attained
without the possibility that the chemical structure of the resin played some part in the
anode kinetics. Second, mercury is known to solvate many plastics on intimate contact,
so that, if a bead were actually to wet the surface, the validity of the analysis would be
questionable. There is good reason to believe that a single ion exchange bead (diameter
less than 2 mm) is of such low density that in water or in $10^{-4}$M HCl it will not by
gravity press down hard enough to actually make contact with the mercury surface. The
case can be understood from the standpoint of the thermodynamics of polymolecular
films (ref. 13, pp. 324 to 332) and is similar to the problem of a bubble of air under
water being pressed to a solid surface. If the film separating the bubble from the sur-
face is dynamically stable, the pressure of this film will exert a force tending to
increase the separation. But for very small thicknesses a region of instability can be
reached, with the pressure even becoming negative. When this occurs, the separating
film will collapse, and the bubble will then adhere to the surface without the aid of an
external force. In the present electrolysis cell, the polarized bead will result in image
forces tending to draw the bead to the anode surface. In addition, the composition of the
aqueous film will undergo change once any electrolysis gets under way. Consequently,
one must be conscious of the fact that the bead in a given experiment could make physi-
10
cal contact with the mercury surface and must design his experiments so that the region around $\theta = \pi$ can be observed. In present experiments it did not appear that any difficulty was encountered in this regard (with one exception to be discussed with experimental results), even when applied voltages were quite large. Photographic and other evidence to this effect will be presented with experimental results.

Necessary or desirable properties of a geometrical, physical, and chemical nature must finally be considered that make a given ion exchange material suitable for present purposes. Geometrically, an ion exchange bead in the form of a smooth sphere is optimum, not just because of the conducting sphere analogy, but, more importantly, from the standpoint in handling of single beads (to be explained in the experimental procedures section) and from the standpoint of the local cell concept with the accompanying anode contact problem. In particular, an irregularly shaped particle with sharp edges would be the least desirable, because here chances would be great for physical contact with the mercury surface. Physical properties include optical transparency, thermal stability in the working temperature range, and freedom from spectrographic interferences. Optical transparency enhances the observation of the phenomena taking place and also serves as a means of establishing whether a bead made physical contact with the mercury surface. (A bead of the material used in these experiments would become opaque with a coating of metallic film if pressed into a mercury surface.) Regarding thermal stability, even though experiments reported herein were carried out in the temperature range of 20° to 25° C, a bead had to be dried at 110° C before spectrographic ignition. However, it should be noted that good thermal stability will permit the microsampling technique itself to be used over a wider temperature range. Also one must seek a material that when ignited will not lead to interferences in the spectrographic detectability of metal species being studied. Such interferences (for the purposes of qualitative analysis) could consist of background radiation at the wavelengths of atomic lines and the too violent decomposition of some resin materials when ignited in a spectrographic electrode. The rapid decomposition of some resin materials could propel a bead out of the spectrographic electrode, thus losing the sample. (Restrictions for quantitative work are even more stringent.) Finally, desirable chemical properties include a high degree of ionization at the exchange sites (required for conductor and mobility properties) and stability of the resin material to oxidation and reduction.

A resin with the desired properties which was selected for this work is Dowex 50W-X8. This is available in the form of transparent spherical beads, which are produced by nuclear sulfonation of a cross linked styrene-divinylbenzene matrix to yield a resin (H form) with the chemical formula $R(SO_3H)_n(H^+)_n$. The sulfonic acid groups ($-SO_3H$), are the exchange sites anchored to the matrix $R$, and $H^+$ is the mobile component. Since this is a strongly acid resin, it is fully ionized and usable over the full pH range available in water solution. Such resin has good thermal stability up to 150° C, is only
slowly oxidized by hot, 15-percent nitric acid, and has a selectivity for metallic ions with $\text{H}^+$ near the bottom of the list. Also, the resin material was found by trial to cause little interference in spectrographic excitation (ref. 1).

EXPERIMENTAL PROCEDURES

Spectrographic Analysis

Spectrographic analyses were carried out using a 1.5-meter grating spectrograph in the wavelength range of 200 to 400 nanometers, with spectra recorded on 35-millimeter photographic film (ref. 14, p. 68). Excitation of samples was carried out with a 220-volt direct-current arc (ref. 14, p. 191) at 10 amperes, using graphite electrode systems shown in figure 5. Elements of concern in this report were detected by the presence of one or more spectral lines whose wavelengths are listed in table I. The

![Diagram of graphite electrode systems used for spectrographic excitation.](image)

(a) Cathode cup system used for analysis of bulk samples. Cup dimensions, 0.48-centimeter (3/16 in.) diameter; 0.32 centimeter (1/8 in.) deep.

(b) System used for analysis of single ion exchange beads. Cavity consists of 0.24-centimeter (3/32 in.) deep cut with No. 50 drill (diam. 1.778 mm).

Figure 5. - Graphite electrode systems used for spectrographic excitation. Direct current ARC, 10 amperes at 220 volts d.c.
TABLE I. - WAVELENGTHS OF ATOMIC LINES USED FOR SPECTRO-

GRAPHIC ANALYSIS

<table>
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<td>Mn</td>
<td>257.6104</td>
<td>2576.104</td>
<td>V₁</td>
</tr>
<tr>
<td>Ni</td>
<td>341.4765</td>
<td>3414.765</td>
<td>U₁</td>
</tr>
<tr>
<td>Pb</td>
<td>405.7820</td>
<td>4057.820</td>
<td>U₁</td>
</tr>
<tr>
<td>Pt</td>
<td>306.4712</td>
<td>3064.712</td>
<td>U₁</td>
</tr>
<tr>
<td>Sn</td>
<td>283.9989</td>
<td>2839.989</td>
<td>U₁</td>
</tr>
</tbody>
</table>

The symbol U₁ indicates a line due to the neutral atom, where U₁ is the most sensitive (what spectroscopists refer to as the "raie ultime"), and U₂, U₃, ... indicate decreasing orders of sensitivity. The symbol V₁ indicates a line due to the singly ionized atom. (Nomenclature follows that in ref. 15.) The most sensitive lines were always used if they were within the working wavelength range of the spectrograph and were not obscured by interferences. For calcium U₁ was rarely used because the short wavelength tail of the graybody radiation continuum was too heavy.
percent transmission (percent T) of each spectral line on a film was used as a qualitative indicator of whether a given species was present in large amounts or in traces. This was recorded by using a photoelectric microdensitometer with a clear portion of the film (as close as possible to the desired line) defined as 100 percent T, and a closed densitometer slit defined as 0 percent T. With the equipment used, a line with 99 percent T represented a lower limit of detectability. A transmission less than 20 percent T represents an overexposure of the film. In this work film densitometry was not used to provide a quantitative analysis for a given species, although occasionally we guessed about relative quantities of two or more species. (This was done by referring results to a calibration where metal ions were placed on ion exchange beads in known concentration ratios.) Quantitative spectrographic analyses can always be carried out by working curve methods, but were not necessary for the work reported herein. For details as to quantitative methods see reference 14.

Preparation of Spectrographically Pure Chemicals

Three reagents of spectrographic purity were needed for the analytical procedures to be described. These are triple distilled water, ultra pure HCl, and cation exchange resin (H form). Triple distilled water was kept in constant supply by the electrochemical laboratory where this work was carried out. A periodic quality control check was performed by the use of a flame photometer that could measure sodium contamination levels of 1 part per billion or less. The water supply contamination never exceeded this level. (For a recent discussion and review of ultra pure water see ref. 16.)

To start out, one must have absolutely clean plastic vessels in which to store triple distilled water, ultra pure HCl, and ion exchange resin. (No glass containers are ever used for reagent storage in this type of work.) The vessels used were polyethylene bottles that had been carefully leached of all traces of metal contaminants with HCl and triple distilled water, to the point where the only level of contamination ever detected was that set by the quality of the triple distilled water itself.

Ultra pure HCl (in triple distilled water) of about 0.1 N was prepared by generating the HCl gas, which was then washed and passed slowly into a polyethylene bottle containing triple distilled water, while stirring with a polyethylene coated magnetic stirring bar. The HCl gas was washed twice after being generated; first by passing through concentrated reagent grade HCl, and then through a small volume of triple distilled water. The latter soon became saturated, and afterwards the rest of the gas passed from this to the collecting bottle. All parts of the washing train were made of polyethylene or Teflon.

Ion exchange resin as received from the manufacturer (H form - beads 20 to 50
<table>
<thead>
<tr>
<th>Ca (422.6728 nm)</th>
<th>Ca (393.3666 nm)</th>
<th>Mg (382.9350 nm, 383.2306 nm, 383.8258 nm)</th>
<th>Na (330.2988 nm, 330.2323 nm)</th>
<th>Longer wavelengths</th>
<th>Shorter wavelengths</th>
<th>Mg (285.2129 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (396.8468 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Iron spectrum for wavelength calibration; (b) Ion exchange resin before purification; (c) Ion exchange resin after purification.

Figure 6. - Emission spectra showing results of purification of ion exchange resin.
mesh) contained several contaminants, the most notable of which were calcium, magnesium, and sodium. Figure 6(b) shows an emission spectrum of the starting material. (This spectrum was the result of igniting a full cup (fig. 5(a)) holding about 40 to 50 beads to a complete burn. The electrode loaded with resin was dried at 110°C for 3 hours before igniting. Molecular bands in the figure are mostly due to CN which results from graphite electrodes being ignited in atmospheric air. These bands are less intense in figure 6(b) than in figure 6(c) because in figure 6(b) the large amounts of easily excited Ca, Mg, and Na drained the available energy from the arc.) This resin is not at first placed into the specially cleaned polyethylene bottles. Rather, the cleaning process is started in another reasonably clean polyethylene container. At first the fresh resin is treated with 0.2 N HCl made from concentrated reagent grade HCl and diluted with ordinary distilled water (not triple distilled). The resin is swirled several times at convenient intervals and allowed to equilibrate with its interstitial liquid for at least a day. The liquid is then decanted as completely as possible by pouring. (This is necessarily a dilution process since one does not want to place any type of filter probe into the resin.) The resin is washed several times with 0.2 N HCl, and a small sample taken for spectrographic analysis. This procedure was repeated until a spectrographic analysis showed that no further gains could be made by using ordinary distilled water. (In this case five treatments were necessary.) The procedure is then continued by using HCl prepared by diluting concentrated reagent grade HCl with triple distilled water, and spectrographically analyzing small samples at each stage of the purification. Nineteen such treatments were necessary before reaching a contamination level where commercial reagent grade HCl could no longer be used. At this point the resin contamination consisted of only a small quantity of calcium. The resin was then put into one of the specially cleaned polyethylene containers (after first washing several times with triple distilled water), and the cleaning process continued using the specially prepared HCl. After eight treatments, the calcium level was reduced to the point where an emission spectrum contained only weak calcium lines (about 80 percent T for U1). It was impossible to remove the last traces of calcium by this washing technique. (However, a single ion exchange bead ignited with the electrode system in fig. 5(b) showed no detectable contamination.) The resin was now washed several times with triple distilled water to remove HCl and was stored in triple distilled water. To remove as much remaining resin electrolyte as possible, the resin was retreated with fresh triple distilled water once a week, for twenty weeks. The resulting resin in the hydrogen form was thus free of all but a faint trace of calcium (fig. 6(c)), and at this point it seems reasonable to assume that the only resin electrolyte remaining was that required for electroneutrality of the exchange sites. (Note: The final leaching of resin electrolyte is not recommended for more resin than can be used over a period of 8 months or so, because the strong electrostatic repulsion at the anchored exchange sites - due to insufficient ionic shield-
ing - can lead to some attritional degeneration. That is, the exchange sites can literally tear themselves away from the plastic matrix by mutual repulsion.)

Purification of Mercury by Calcium Dispersion

A purification process for liquid mercury referred to herein as calcium dispersion was developed by a coworker (ref. 6) at the same time the present research was being carried out. This process is not adaptable to the study of bound states or surface concentration, but, in addition to being a purification process, it is able to detect the presence of contamination in mercury at levels well below the sensitivity of other known methods of analysis. If one dissolves \( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \) in methanol and, from the resulting methanol solution (which may be made slightly acid with HCl - amount not critical), electroplates calcium into mercury (at 8 to 10 V dc), what is presumably a fine dispersion of calcium or calcium amalgam is formed. The methanol solution is now decanted, the mercury washed several times with methanol, and the mercury finally dried by touching filter paper to the surface. If left standing (about 12 hr), the dispersion will concentrate at the surface forming a dull gray crust that is easily removed. When this crust is subjected to an emission spectrographic analysis (electrode system in fig. 5(a)), one finds that it contains not only mercury and calcium, but also impurities that were present in the mercury. Moreover, spectrographic analysis of the mercury under the crust indicates that the surface concentration of the calcium dispersion is almost quantitative. (Calcium can be detected spectrographically in mercury by direct arcing to \( 10^{-5} \) to \( 10^{-6} \) percent by weight, or \( 10^{-7} \) percent using an inert atmosphere (ref. 6, p. 43).) In this way contamination was found even in the best mercury obtainable from commercial sources.

With regard to mercury purification in general, one often encounters the belief that if mercury "bubbles" when shaken under water, this is a criterion of its purity. In fact, such criterion is often used in standard wet methods of purification. Our experiences with the calcium dispersion process indicate that this belief is unfounded and that such bubbling can at best be taken as a criterion of homogeneity. Immediately after plating calcium into mercury, the latter would bubble under methanol in exactly the same way. This ability to bubble stopped, however, as soon as surface concentration started.

Preparation of Mercury Samples for Bead Analysis

Mercury aliquots were subjected to two types of electrochemical treatment in preparation for a bead analysis experiment. These were an attempted high-voltage stripping of contaminants and the deliberate addition of contaminants. (All data tabulations
to be presented will state whether one, both, or neither was used for each individual case. These preliminary treatments were carried out in a Teflon container using platinum wire electrodes that were flame sealed in polyethylene tubing with only the wire tip exposed. Spectrographic analysis showed that the platinum wire used was not a source of contamination.

High-voltage stripping consisted of applying 250 volts (dc) to a mercury sample covered with spectrographically pure $10^{-4}$M HCl (Hg the anode). The container was gently swirled during this process to facilitate mixing. After 5 minutes of electrolysis the HCl was decanted, the mercury washed several times with $10^{-4}$M HCl, and a second stripping applied. This was repeated three times, after which the mercury was finally washed several times with $10^{-4}$M HCl and used as desired.

Deliberate addition of contaminants consisted of the high-voltage electroplating of a given metal species into the mercury from a salt containing the species. A known quantity of reagent grade salt was dissolved in triple distilled water for this purpose. Concentrations of contaminants listed in tabulations of data are to be interpreted as maximum concentrations that would have resulted were the electroplating 100 percent efficient. Voltages used for this electroplating were either 90 or 250 volts (dc) applied for 15 minutes. None of the results appeared to be influenced by which voltage had been used. After electroplating, the mercury aliquot was washed several times with triple distilled water, and a small portion of this aliquot was immediately loaded into the electrolysis cell to be described.

Special Equipment and Procedures

A diagram of the electrolysis cell used in bead electrolysis experiments is shown in figure 7. Figure 8 shows the cell with a microscope-camera arrangement that was used to photograph the bead and mercury surface. The Teflon base of the cell was machined to fit the heavy wall glass capillary tube tightly. When not in use the capillary tubes were stored in a polyethylene bottle filled with triple distilled water. To prevent a mercury sample from becoming exposed to a glass surface during an analysis (or exposed to HCl that is in turn exposed to glass), just before use a capillary tube was dried with acetone, washed with an acetone-Lucite solution (1 g Lucite/100 cm$^3$ acetone) and dried with a stream of high purity nitrogen. This leaves a thin transparent film of Lucite on the wall of the capillary tube, so that the loaded electrolysis cell has a cross section like that shown in figure 9. To assemble the cell for an experiment the Teflon base was first filled with HCl. The capillary tube was then pushed into the base, forcing the HCl up the tube without entrapment of air bubbles. Mercury was then placed in the cell, a little at a time, using a polyethylene capillary dropper similar to that shown in figure 10.
Figure 7. - Diagram of electrolysis cell.
Figure 8. - Experimental assembly.

Figure 9. - Cross section of loaded electrolysis cell showing method of isolating mercury sample from glass wall of capillary tube.
After each addition of mercury, the cell was tapped gently to make the mercury displace the HCl and travel to the bottom of the cell. In this way the cell was loaded with sample mercury to a column height of 4.44 centimeters (1.75 in.) above the Teflon base. An ion exchange bead was finally selected using a polyethylene capillary dropper (fig. 10) and placed in the cell. (This was not the same dropper used to handle mercury samples.) An effort was made to select beads large enough to minimize the clearance between the bead and capillary wall. On completion of an electrolysis, a bead was extracted from the cell with the same dropper, placed in the cavity of a graphite electrode shown in figure 5(b), dried for 3/4 hour at 110° C, and subjected to spectrographic analysis. When not in use, all utensils were stored in triple distilled water. Bead electrolysis experiments were performed at applied voltages of 1.72, 3.00, and 90 volts (dc). The lowest of these is more than enough to exceed the "absolute" potentials in the electromotive series of any of the species of major concern for present experiments. For some but not all of the experiments a galvanometer was available for measuring the current drawn by the cell. These currents are included with experimental data.
DEFINITION OF MERCURY SAMPLES

Two bulk samples of mercury henceforth referred to as "bulk sample A" and "bulk sample B" were used for present experiments.

**Bulk Sample A**

Bulk sample A consisted of 1/4 liter of instrument grade mercury ($<10^{-4}$ percent by wt. foreign metals) that had been left standing (dry) undisturbed for about a year and a half. (This was actually part of a supply of virgin mercury that had been secured for the work of ref. 5.) The container was made of a high purity glass, that was subjected to a spectrographic analysis after this work had been completed and found not to be a source of impurities found in the mercury. Physical dimensions of bulk sample A were that of a square column approximately 10 centimeters high, with a top surface area of about 25 square centimeters. Two kinds of aliquots were taken from this sample for bead analyses: one kind from the surface and the other from the center. Unless otherwise noted these were 1-cubic-centimeter aliquots extracted with a high purity glass pipette fitted to a syringe. A surface aliquot was extracted from the bulk sample by touching the tip of the pipette to the surface just enough to make a slight indentation, and drawing up on the syringe plunger. A spectrographic analysis using the electrode system in figure 5(a) was performed on each aliquot as extracted. The analysis consistently showed contamination levels to be below the limits of spectrographic detectability. (Of course, this procedure resulted in the mixing of the aliquot so extracted. However, the purpose of experiments with bulk sample A was not to study suspected surface concentration as such, but to establish the validity of the local cell concept and its possible application to such study.)

**Bulk Sample B**

Bulk sample B was the result of subjecting a 5-pound flask of U.S. P. grade triple distilled mercury ($<0.004$ percent by wt. foreign metals) to successive applications of the calcium dispersion process. (It is necessary to mention in passing that this process had not been worked out until most of the experiments with bulk sample A were completed.) Table II lists the results of these successive applications (about 1/2 mole of calcium electroplated in each step). (Spectrographic analysis of the starting mercury showed only a trace of silver.) After the sixth application the mercury was collected in a polyethylene bottle filled with triple distilled water and stored in this way. This results in the mercury being isolated from the container walls by a thin film of water.

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### TABLE II. - IMPURITIES DETECTED IN SUCCESSIVE APPLICATIONS OF CALCIUM DISPERSION PROCESS IN PREPARATION OF BULK SAMPLE B<sup>a</sup>

<table>
<thead>
<tr>
<th>Step</th>
<th>Spectrographic analysis of calcium crust</th>
<th>Spectrographic analysis of underlying mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ag (very strong)</td>
<td>Ag (weak)</td>
</tr>
<tr>
<td></td>
<td>Au (strong)</td>
<td>Ca (weak)</td>
</tr>
<tr>
<td></td>
<td>Cu (strong)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg (weak)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb (strong)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt (strong)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ag (moderate)</td>
<td>Ca (trace)</td>
</tr>
<tr>
<td></td>
<td>Au (weak)</td>
<td>Mg (trace)</td>
</tr>
<tr>
<td></td>
<td>Cu (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sn (weak)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ag (strong)</td>
<td>Ca (trace)</td>
</tr>
<tr>
<td></td>
<td>Au (trace)</td>
<td>Mg (trace)</td>
</tr>
<tr>
<td></td>
<td>Cu (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt (weak)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ag (strong)</td>
<td>Ca (trace)</td>
</tr>
<tr>
<td></td>
<td>Au (trace)</td>
<td>Mg (trace)</td>
</tr>
<tr>
<td></td>
<td>Cu (moderate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt (weak)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ag (trace)</td>
<td>Nothing</td>
</tr>
<tr>
<td></td>
<td>Cu (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt (trace)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Ag (trace)</td>
<td>Nothing</td>
</tr>
<tr>
<td></td>
<td>Cu (trace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg (trace)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Traces of Cu and Mg were present as contamination in the calcium chloride used for the calcium dispersion process, although it is doubtful that this could account for all the Cu observed in steps 1 to 4.
(More elaborate methods of storing mercury to avoid exposure to oxygen that can diffuse through plastic container walls were investigated, and are discussed in ref. 6. However, with bulk sample B stored as indicated, there was no noticeable oxide formation during the time (3 months) in which experiments with this sample were carried out.) The final contamination level in bulk sample B could not be determined, but based on work using added contamination, a level much less than $10^{-6}$ percent by weight is quite probable.

**EXPERIMENTAL RESULTS**

**Experiments with Bulk Sample A**

Experiments performed with aliquots from the surface and center of bulk sample A are summarized in table III. Entries corresponding to surface samples are presented in the same order in which the experiments were performed. A comparison of successive entries in this table indicates that there was some surface concentration of contaminants in bulk sample A. This indication establishes the ability of the microsampling technique to detect this fact. (However, no contamination of aliquots as extracted from bulk sample A could be detected with the spectrograph.) For example, entry 1 indicates a concentration of Ag near the surface, and entry 2 a concentration of Ca, Cu, and Mg just below the surface. Further under the surface, the only electrolyzable species is Hg itself (entry 4). Entry 3 is the result of a control experiment where an attempt was made to remove all contaminants from an aliquot before the bead analysis. The fact that only Hg was detected in this case establishes that the contaminants observed actually came from the mercury surface and were not due to faulty technique. Entry 5 establishes lower detectability limits for contaminants deliberately added to the mercury of bulk sample A. The most intriguing results are given in entries 6 and 7. These indicate the possibility of molecular structure with very strong orientation tendencies at the mercury surface. For example, the experiments in entry 7 are compatible with the idea that a bound state species consisting of copper, silver, and mercury was formed with a structure such that the copper part is quantitatively oriented upward, provided the metal surface is uncharged or carries at most a small positive charge. As the positive charge at the surface is increased, this orientation is reversed with the silver-mercury part of the structure oriented upward (fig. 11). Furthermore, the bond linking copper to the rest of the structure appears to be weak enough (at least for a few hours after the copper-silver addition to the aliquots) so that either the copper part can be dislodged from the surface leaving the silver-mercury part behind, or the silver-mercury part can be dislodged leaving the copper behind. Such structure is also compatible with entry 1 where copper alone was plated into the aliquot, but apparently some
### Table III - Bead Analyses of Aliquots from Bulk Sample A

<table>
<thead>
<tr>
<th>Entry</th>
<th>Source of added contamination</th>
<th>Maximum concentration of added contamination, percent by weight</th>
<th>Voltage applied to cell</th>
<th>Current A initial-final</th>
<th>Duration of electrolysis, hr</th>
<th>Spectrographic analysis of bead component, percent T[^b^]</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl₂ · 2H₂O</td>
<td>0.1</td>
<td>1.72</td>
<td>NM[^b^]</td>
<td>1.0</td>
<td>(Hg. 66) (Cu. 59) (Ag. 63) (Ca. 2.6)</td>
<td>Preliminary experiment whose purpose was to test the general validity of the local cell concept. In this trial it appeared that the bead made physical contact with the anode surface. Bead became opaque from single point of contact, and slowly working up to top. Spectrographic analysis was with electrode system shown in fig. 5(a). Content of Hg in bead was estimated to be in the same order as the combined Cu, Ag content, with Cu = Ag (atomic ratio).</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>1.72</td>
<td>NM[^b^]</td>
<td>2.25</td>
<td>(Hg. 66) (Cu. 59) (Ag. 63) (Ca. 2.6)</td>
<td>Top hemisphere of bead became slightly “fogged”, while bottom hemisphere remained relatively clear. Elastic straining (fig. 13(a)) indicates that bead may have come much closer to anode surface (without wetting) than was the case in any other subsequent low-voltage experiment. All calcium lines were obscured by CN bands. Datum is for Ca (393.3666 nm).</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>3.00</td>
<td>2.8 0.1</td>
<td>2.50</td>
<td>(Hg. 63)</td>
<td>Purpose of experiment was to establish that species detected on bead came from anode surface and were not the result of faulty technique. Aliquot was 50 grams.</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>1.72</td>
<td>2.0 0.4</td>
<td>3.00</td>
<td>(Hg. 64)</td>
<td>Experiments establish that only electrolyzable species from center of bulk sample A is mercury. High-voltage experiments here were characterized by much more vigorous activity around $\theta = \tau$ than was the case when contaminants were added (see entry 7).</td>
</tr>
<tr>
<td>5</td>
<td>CuCl₂ · 2H₂O</td>
<td>1.0 x 10⁻⁶</td>
<td>1.72</td>
<td>5.0 1.6</td>
<td>1.50</td>
<td>(Cu. 65) (Mn, 96) (Mg. 99) (Cu. 59) (Ag. 95) (Ca. 98)</td>
<td>Experiment establishes lower limits of detectability for contaminants freshly added to mercury and indicates that the total absence of one or more species at higher levels of contamination (see entries 6 and 7) is not the result of a lack of sensitivity. Bead in this experiment became distinctly “fogged” on the top hemisphere. This fogging shows up in the photographs as a pitted appearance that develops with time (see fig. 13(b)). Aliquot was 100 grams.</td>
</tr>
<tr>
<td>6</td>
<td>CuCl₂ · 2H₂O</td>
<td>0.1</td>
<td>1.72</td>
<td>4.8 1.2</td>
<td>1.50</td>
<td>(Hg. 65)</td>
<td>Surface of unused portion of aliquot had a shiny silver-like luster after the copper was added, which remained unchanged for a duration comparable to that of similar observations for entry 7.</td>
</tr>
<tr>
<td>7</td>
<td>Cu(NO₃)₂ · 3H₂O</td>
<td>0.05</td>
<td>1.72</td>
<td>3.7 0.6</td>
<td>1.50</td>
<td>(Cu. 15)</td>
<td>Samples were extremely shiny when first prepared, and remained so during the electrolysis experiments. But the unused portion of each aliquot, when left standing overnight, was found to have a surface film of bright copper-colored luster. After standing for 2 more days, such film would disappear, the normal &quot;silver&quot; appearance of mercury being all that remained. A study of the evolution of this phenomenon with successive bead analyses was not carried out because of time limitations when this research was done and because of the availability of only one electrolysis assembly.</td>
</tr>
</tbody>
</table>

[^b^]More than 1 percent T represents results in duplicate runs. (Note: In ref. 1 only one experiment of each type is discussed. These represent cases where printable photographs of ion exchange beads were obtained.) Duplicate runs were always on different aliquots from bulk sample A.

[^c^]NM indicates current not monitored; galvanometer was not always available for these experiments.

[^d^]High voltage stripping of aliquot before addition of contaminants and or bead analysis.

[^e^]See table IV.
silver was already present as a surface concentrated contaminant. Since the bead in experiment 1 was probably wetted by the surface, the three-species structure could have been electrostatically pulled onto the bead intact. Likewise entry 6 would appear to be compatible with a bond formation involving copper and mercury, with the mercury oriented upward. It is unlikely that the lack of appearance of one or more species in entries 6 and 7 can be accounted for by lack of sensitivity, because these experiments were deliberately carried out at concentration levels four to five orders of magnitude above the demonstrated detectability limits. Also, it must be emphasized that these hypotheses regarding structure can only be made for species just after their addition to the mercury of bulk sample A. The observation in table III entry 7 together with results to be presented shortly indicate that any structures that are formed are likely to be

![Diagram of orientation of Ag,Cu,Hg bound state at mercury surface.](image)

**Figure 11.** - Orientation of Ag,Cu,Hg bound state at mercury surface.

With mercury surface uncharged, transparent bead acts as a convex lens. Light rays incident upon its periphery are refracted through an angle too great to enter microscope.

When mercury surface becomes charged, electrical forces deform bead in region \( \theta = \pi \), resulting in a distorted image.

**Figure 12.** - Explanation of photographs of ion exchange beads (fig. 13).
changing with time. Further speculations about possible molecular structures and reaction mechanisms are given in appendix B.

Photographs of ion exchange beads (fig. 12) in several experiments are shown in figure 13, where an effort was made to include examples representative of the entire spectrum of observations. These are essentially shadow photographs, with the transparent ion exchange beads acting as spherical lenses. Generally the beads were small enough so that they rested to one side of the cell, and hence did not permit the point of closest approach to be photographed through the microscope. An exception was the unusually large bead specimen shown in figure 13(c), where the separation from the anode surface shows up clearly. Any flow channels that develop between the anode surface and the bead show up as shadows, the same as does the periphery of a bead, because such regions are essentially cylindrical lenses formed by a medium with an index of refraction different from that of the surrounding environment. Hence, incoming light is refracted away from the line of sight of the microscope. In some of the frames a dot or circle shows up in the center of the bead. This is an image of the light bulb used for illumination. Elastic deformations that show up in images of polarized beads have two possible causes: one due to electrostriction, that is, the phenomenon whereby an elastic body is elongated in the direction of the electric field (refs. 9 to 11), and the second due to metallic ions flowing onto the bead. The former would be expected to increase in intensity as electric forces increase, and hence is an indicator of how close the bead came to the mercury surface, as well as being a function of the applied voltage. The part of the deformation due to metallic ions is the result of ionic shielding at the exchange sites different from that provided by $H^+$. This alters the forces of mutual repulsion of the anchored exchange sites themselves. The sequence shown in figure 13(a) was unique for low-voltage experiments, in that the strong elastic deformation near $\theta = \pi$ resembles that only achieved normally at high voltage. This may indicate that the bead came closer than usual to the anode surface due to the particular contaminants that happened to be present. Of the high-voltage experiments, those where nothing was added to mercury evidenced much more vigorous activity around $\theta = \pi$ than when contaminants were added. The sequence in figure 13(d) shows particularly well such vigorous activity and also the strong tendency to keep localized around $\theta = \pi$.

Whenever the galvanometer was used to measure currents, one could detect a relaxation time in the cell after the circuit was closed that was several seconds longer than if the same voltage were applied to a cell without the bead. However, polarization of the cell was always complete in less than 10 seconds. Table IV lists an example of typical currents drawn by an electrolysis cell in low voltage experiments. Finally it should be noted that with the lone exception of experiment 1, there appeared to be no trouble with the bead making intimate contact with the anode surface (that is wetting as distinguished from a very close approach without wetting). A bead could be made to wet the surface if it were deliberately pressed to the mercury surface and held down for
Low Voltage Experiments

(a) Sequence corresponding to table III, entry 2. (1) Bead before closing circuit; (2) bead 5 minutes after closing circuit. Strong deformation in this case was unique for low voltage experiments, indicating a closer than usual approach to mercury surface.

(b) Sequence corresponding to table III, entry 5. (1) Bead before closing circuit; (2) bead 25 minutes after closing circuit; (3) bead 4.17 hours after closing circuit; (4) bead 17.17 hours after closing circuit.

(c) Sequence corresponding to table III, entry 7 (low voltage) showing separation of bead from mercury surface. (1) Bead before closing circuit; (2) bead at end of electrolysis (potential still applied). Bead in this sequence was elastically strained.

Figure 13. - Photographs of ion exchange beads in electrolysis cell.
High Voltage Experiments

(d) Sequence corresponding to Table III, entry 4 (high voltage). (1) Bead before closing circuit; (2) bead 10 minutes after closing circuit; (3) bead 12 minutes after closing circuit (note flow channel that develops to side of $e = \pi$. On the top of the bead is a bubble of H$_2$ gas that was shot down from the primary cathode.)

(e) Sequence corresponding to Table III, entry 7 (high voltage). (1) Bead before closing circuit; (2) bead 3 minutes after closing circuit; (3) bead 20 minutes after closing circuit; (4) bead 5 minutes after circuit was broken (note elastic relaxation).

Figure 13. - Concluded.

TABLE IV. - OBSERVED CURRENTS IN ELECTROLYSIS CORRESPONDING TO TABLE III, ENTRY 5

<table>
<thead>
<tr>
<th>Time, min.</th>
<th>Current, $\mu$A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>----</td>
</tr>
<tr>
<td>5</td>
<td>7.90</td>
</tr>
<tr>
<td>10</td>
<td>6.31</td>
</tr>
<tr>
<td>20</td>
<td>4.84</td>
</tr>
<tr>
<td>25</td>
<td>2.95</td>
</tr>
<tr>
<td>70</td>
<td>1.48</td>
</tr>
<tr>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>240</td>
<td>.77</td>
</tr>
<tr>
<td>1030</td>
<td>.26</td>
</tr>
<tr>
<td>2900</td>
<td>.23</td>
</tr>
</tbody>
</table>

*aJust after closing circuit.
several seconds before starting the electrolysis. But then the bead (which became opaque) would also tend to cling to the anode surface when an attempt was made to extract it from the cell.

**Experiments with Bulk Sample B**

As mentioned earlier, the calcium dispersion process was not available until after most of the experiments with bulk sample A had been completed. Consequently, these were done with the assumption that at least the center of the sample consisted of uncontaminated mercury. However, as table II shows, even platinum can be found as a trace contaminant, and this fact raises an uncertainty when platinum wire electrical contacts are used in an electrolysis cell. As a result, a new cell design shown in figure 14 was used for experiments with bulk sample B. This cell has the advantage of simplicity: it eliminates the necessity of coating a capillary tube with a film of lucite, and, in addition, it eliminates the necessity of having a platinum wire in contact with the mercury except during the time when an electrolysis is being performed (an advantage if a sample is to stand for some time before performing a bead electrolysis). The entire cell was housed in a desiccator equipped with a side arm through which electrical contacts were made. The atmosphere inside the desiccator was equilibrated with $10^{-4}$ M HCl to prevent excessive evaporation from the cell itself.

![Figure 14 - Electrolysis cell used for experiments with bulk sample B.](image-url)
Results of experiments with bulk sample B are given in table V. With sample 1 it is evident that the mercury obtained from the calcium dispersion process was clean but not perfect. Consequently, with samples 2 and 3 an attempt was made to strip the last traces of contaminants free from the mercury before performing a bead electrolysis. When this was done the results were not only surprising but were apparently in contradiction with results from bulk sample A. Nothing could be electrolyzed onto a bead at low voltage, and only mercury together with other contaminants at high voltage. The source of the currents in the cell could not be traced to any leakage path and may have

TABLE V. - OBSERVED CURRENTS AND RESULTS OF BEAD ANALYSES FOR ALIQUOTS FROM BULK SAMPLE B

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current, μA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>2.18</td>
<td>6.49</td>
<td>130</td>
</tr>
<tr>
<td>1</td>
<td>NR^b</td>
<td>NR</td>
<td>348</td>
</tr>
<tr>
<td>5</td>
<td>NR</td>
<td>2.95</td>
<td>42</td>
</tr>
<tr>
<td>10</td>
<td>1.42</td>
<td>NR</td>
<td>7.1</td>
</tr>
<tr>
<td>15</td>
<td>NR</td>
<td>2.06</td>
<td>NR</td>
</tr>
<tr>
<td>20</td>
<td>.55</td>
<td>.65</td>
<td>1.7</td>
</tr>
<tr>
<td>30</td>
<td>.55</td>
<td>NR</td>
<td>.1</td>
</tr>
<tr>
<td>40</td>
<td>.52</td>
<td>NR</td>
<td>-----</td>
</tr>
<tr>
<td>50</td>
<td>.51</td>
<td>NR</td>
<td>-----</td>
</tr>
<tr>
<td>65</td>
<td>.51</td>
<td>NR</td>
<td>-----</td>
</tr>
<tr>
<td>115</td>
<td>NR</td>
<td>.71</td>
<td>-----</td>
</tr>
<tr>
<td>155</td>
<td>.51</td>
<td>NR</td>
<td>-----</td>
</tr>
<tr>
<td>225</td>
<td>.51</td>
<td>NR</td>
<td>-----</td>
</tr>
<tr>
<td>235</td>
<td>NR</td>
<td>.75</td>
<td>-----</td>
</tr>
<tr>
<td>285</td>
<td>.65</td>
<td>NR</td>
<td>-----</td>
</tr>
<tr>
<td>320</td>
<td>NR</td>
<td>.90</td>
<td>-----</td>
</tr>
<tr>
<td>465</td>
<td>.65</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>615</td>
<td>c.67</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment before electrolysis</th>
<th>Voltage applied to electrolysis cell, V</th>
<th>Spectrographic analysis of bead, (element, % T of line)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>3.00</td>
<td>{(Hg, 30) (Ca, 95) (Cu, 75) (Mg, 97)}</td>
</tr>
<tr>
<td>2</td>
<td>High voltage stripping</td>
<td>3.00</td>
<td>Nothing</td>
</tr>
<tr>
<td>3</td>
<td>High voltage stripping</td>
<td>90.0</td>
<td>{(Hg, 28) (Ag, 96) (Cu, 96)}</td>
</tr>
</tbody>
</table>

^a Just after closing circuit.
^b NR indicates current not recorded at this point.
^c Electrolysis terminated at this time.
been due to oxidation or reduction of the resin material of the bead itself in the absence of other electrolysis. (However, the beads did not appear to be unusual after an electrolysis, and H₂ gas was always evolved at the primary cathode as before.) These results were confirmed by several repetitions, and indicate the possibility that the oxidation of mercury itself (Hg - 2e⁻ → Hg²⁺) may be impossible (under comparable circumstances). The last traces of contamination could never be stripped completely from aliquots of bulk sample B, and all indications seem to point to the possibility that the oxidation of mercury itself may require the presence of at least traces of contamination, that is, the oxidation mechanism involves a bound state mercury species.

Calcium Dispersion Analysis of Bulk Sample A

The results with bulk sample B immediately raise the question of why mercury itself could be so easily electrolyzed onto an ion exchange bead from aliquots of bulk sample A (table III, entries 3 and 4). Consequently, a calcium dispersion analysis was performed on a (center) aliquot of bulk sample A, and yielded the following results:

- Ag (very very strong)
- Au (very very strong)
- Ba (weak)
- Bi (weak)
- Co (weak)
- Cu (strong)
- Li (trace)
- Mg (weak)
- Ni (moderate)
- Pb (moderate)
- Pt (moderate)

Of these, only Cu and Mg could be traced to possible contamination of the reagents used in performing the calcium dispersion analysis.

The appearance of silver as a contaminant raises a further question about the results in table III, entry 6, namely, why at least some copper was not observed (as in entry 7) when copper alone was added. One possible answer could be that the silver in this case was in a different kind of bound state than when copper and silver were freshly added together and, hence, was not available to form the bound state observed in entry 7. Another possibility might be that different electrode kinetics transpired when Cu(NO₃)₂ · 3H₂O rather than CuCl₂ · 2H₂O is used as a source of copper. To check the latter possibility copper was now added to an aliquot of bulk sample A from the nitrate dissolved in triple distilled water to a maximum copper content of 0.1 percent by weight. Almost immediately after this was completed a copper colored film appeared.
on the mercury surface. A little of this was scraped off the surface and subjected to a spectrographic analysis, revealing the presence of large amounts of copper and mercury together with a moderate amount of gold. Upon standing overnight this film became a dark scum with the same composition. When left standing several more days, this scum appeared to redissolve somewhat in the sample, but never as completely as with the Cu, Ag, Hg system (table III, entry 7). No such results could be obtained when CuCl₂ · 2H₂O was the source of copper, thus confirming the observation in table III, entry 6. Consequently, it appears that bound states with mercury may depend not only on what other contaminants are present (and for how long), but on the very source of a single contaminant itself.

CONCLUDING REMARKS

Even though the experiments reported herein have some negative overtones, they have nevertheless made at least three positive contributions toward the understanding of trace element effects in liquid mercury and perhaps the nature of metallic bonds. First, they point to a likely source of much of the untidiness that characterizes efforts to study trace element effects in a liquid metal like mercury; second, they provide a means of removing much of this untidiness, thus defining the problem and permitting research to proceed on a more sure footing; and third, they provide a rather inexpensive technique for obtaining information about molecular structure at a metal surface, especially when that structure involves interactions of a metal with trace contaminants. As a starting point for research with liquid mercury, it is evident that a supply of the metal is needed with a contamination level much less than instrument grade mercury (<10⁻⁴ percent by wt. foreign metals). It is likely that the calcium dispersion process can fulfill this need, although it is unknown just what lower limit of contamination can be achieved. However, it is evident from the results from bulk sample B that contamination was reduced to the point where the oxidation properties of mercury are significantly influenced.

Until now there have been three common techniques for the direct observation of molecular structure of metal films. These are X-ray, neutron and electron scattering, with the first being the most common (ref. 2, p. 389). In contrast to the bead electrolysis proposed in this report, all of these methods require the availability of rather elaborate and expensive instrumentation. Although an emission spectrograph is needed for the proposed method, this is only at the last step, and for a period of time long enough to ignite the sample. (The need to leave a mercury sample undisturbed in the experimental apparatus for long periods of time in order to study rates must be considered.) The proposed method does not of course replace any of the other three; it merely approaches the problem of structure differently, and hence is capable of asking
and answering different kinds of questions than may be possible with the other tech-
niques. In addition to being applicable to studies at trace concentrations, the directness
and simplicity of the method results in the advantage that very little theory building is
needed to get from the experimental data to an interpretation of results.

The kinds of questions the bead analysis is capable of answering with regard to
mercury may have a direct relevance to problems encountered when this metal is in-
corporated into electrical networks. Such networks range from a simple mercury
switch, to mercury arcs and vapor lamps, to the use of mercury as a propellant in ion
propulsion engines. Problems in these applications range from the fouling of electrical
contacts by the wetting properties of mercury, which appear to be unrepeatable and
subject to change with time, to the occurrence of unpredictable changes in the charac-
teristics of a given electrical network. It is often suspected that such problems arise
from changes in surface tension properties of mercury due to traces of contamination,
which past experience indicates can be very significant (ref. 3, ch. 10). But at the
same time, attempts to correlate measurements of surface tension with wetting prop-
ties of mercury in electrical circuits often result in confusion. An example of one
possible source of such confusion is provided by the Ag, Cu, Hg system studied in this
report. For suppose one were to measure surface tension properties due to this bound
state for the uncharged metal surface (where the copper end is outward normal to the
surface). These measurements may have little relevance to the situation where that
surface either becomes an electrode itself or approaches another electrode surface
because the molecular structure can rotate, leaving the silver-mercury end outward
normal to the surface. In addition, it is evident that such structure can change with a
rate measured in terms of days, weeks, and even longer. Consequently, not only
molecular structure as a function of electrical surface charge must be considered, but
also the time dependence of such structure, for the problem of designing reliability into
a given electrical network necessitates a knowledge of possible structural changes that
might occur and also a knowledge of how such changes can be controlled. It would
appear that some of these problems of molecular structure at a mercury surface as a
function of electrical charge are of a nature ideally suited to the present microsampling
technique. In the present experiments it would of course have been pointless to continue
extensive investigations with bulk sample A, because of the uncertainties posed by trace
contamination that was ultimately found. But in a controlled experiment one should be
able to study a strongly oriented structure like that of the Ag, Cu, Hg system all the
way from very small applied voltages, through a transition where the structure would be
expected to start rotating, up to large voltages where the rotation is complete. The
present report merely indicates some of the possibilities of what could be done. Definitive results and a full assessment of what can be learned must await the outcome of further research.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 27, 1971,
132-15.
APPENDIX A

SYMBOLS

\( \vec{E} \)  vector electric intensity
\( g \)  electrical conductivity
\( \vec{j} \)  vector current density
\( U_j \)  spectral emission line due to neutral atom
\( V \)  electric potential
\( V_j \)  spectral emission line due to singly ionized atom
\( \nabla^2 \)  Laplacian operator
\( \epsilon \)  permittivity
\( \theta \)  colatitude in spherical polar coordinates
\( \kappa \)  dielectric constant
\( \nu \)  frequency
\( \rho \)  volume density of charge
\( \sigma \)  surface density of charge
\( \varphi \)  longitude in spherical polar coordinates
APPENDIX B

SPECULATION ABOUT MOLECULAR STRUCTURE AND ELECTRODE REACTIONS

In this appendix an attempt is made to construct a molecular model for bound state relationships between liquid mercury and traces of silver, gold, and copper. This is to be understood as only a working hypothesis, that is, as a set of hypothesized molecular structures, which, if they did exist, would be expected to exhibit properties compatible with the experimental observations in the text. No claim is being made for uniqueness of these structures, since there may well be other possibilities in addition to, or instead of, those being considered. However, I believe that the presentation of a molecular model at this time could serve the useful purpose of stimulating further ideas of either an experimental or a theoretical nature, and hence contribute eventually to a better understanding of trace element effects in mercury.

As a preliminary to constructing a molecular model for electrode reactions, consider the saturated calomel electrode commonly used in electrochemical work, whose reversible half cell reaction is usually written as

\[ \text{Hg}_2\text{Cl}_2 + 2e^- = 2\text{Hg} + 2\text{Cl}^- \]

The structure of calomel has long been recognized to involve a metal-to-metal bond, Cl-Hg-Hg-Cl, (ref. 8, pp. 436-7). Since this is a four-atom species, it must be formed in the electrode reaction by either two-, three-, or four-body encounters. Of these, a collision mechanism involving the first possibility is the most reasonable because of the fact that an efficient reaction mechanism is needed for the conversion of reactants to products (and vice versa) in a reversible cell. A two-body encounter mechanism for the formation of \( \text{Hg}_2\text{Cl}_2 \) can be constructed if one assumes that Hg atoms already exist at the metal-solution boundary as metallic bonded diatoms, Hg-Hg. (This does not rule out a coexistence with atomic Hg and/or higher correlations.) Such assumption is reasonable, since the diatomic \( \text{Hg}_2 \) with a ground state dissociation energy of 0.060 electron volt is known to exist in the gas phase (ref. 17, p. 537). If the existence of \( \text{Hg}_2 \) is granted, then the formation of calomel can be viewed as a two-step process whereby Cl\(^-\) is first oxidized to form the diatomic Cl\(_2\),

\[ 2\text{Cl}^- - 2e^- = \text{Cl}_2 \]

followed immediately by a diatom-diatom encounter accompanied by electron transfer,
The molecular model for electrode reactions that will now be constructed is based on three assumptions:

(1) Mercury exists at a metal-solution boundary as the diatom \( \text{Hg-Hg} \).

(2) Metal species when being electrolyzed either into or out of mercury (including mercury itself) exist as short-lived reaction intermediates in the form of metallic bonded diatoms

\[
2[M^{n+}]_{\text{sol}} + 2\text{ne}^- = M-M
\]

(3) Single bond metallic radii and integral valences for hyperelectronic atoms (ref. 8, p. 420) are involved in metallic bonding between Hg and the elements Ag, Au, Cu.

In the scheme on which assumption (3) is based, one has the elements Ag, Au, Cu with possible (integer) metallic valences 1, 3, 5, 7; Cd, Hg, Zn with valences 2, 4, 6; Ga, In, Tl with valences 1, 3, 5; and Ge, Pb, Sn with valences 2, 4. (This is not an exhaustive list of possible valences for these elements.) The bond orbitals involved are \( p, sp^3 \), and \( sp^3 \) with some \( d \) contribution, with bond numbers most commonly divided to correspond to ratios of small integers such as \( 1/4 \), \( 1/3 \), \( 1/2 \), \( 2/3 \). It is perhaps significant that Ag, Au, and Cu occur together in this scheme, since it was found that these three elements were the strongest contaminants in both bulk sample A and bulk sample B, with Ag and Cu being the most difficult to remove. (In this context it might also be well to note that the electronegativities of Ag, Cu, and Hg in their common oxidation states are about the same, whereas that of Au in significantly higher, ref. 8, p. 93.) As found in nature, Cd, Cu, and Zn are very common contaminants in mercury. Of these, Cd and Zn were never encountered in this work. I suspect that these are probably effectively removed from mercury by standard wet methods of purification.

In considering possible structures for the Ag, Cu, Hg system (fig. 11), it is necessary to account for the fact that the atomic species were likely present in the ratios 1:1:2, respectively, (table III, entry 1), as well as the facts that the structure is strongly oriented, that it can rotate in response to an electric charge, and that the bond to copper is likely to be a weak link. Also it is probable that a rapid mechanism is required for formation of this bound state, since it was evidently present only minutes after addition of contaminants. This implies that complicated structures requiring either multiple encounter collision mechanisms or long-range order are to be rejected. Of the integer valences 1, 3, 5, 7 for Cu and Ag, it must finally be noted that the latter three are...
prime numbers (divisible only by themselves or unity). Hence, for a structure to be compatible with even integer valences for Hg, as well as the simple ratio division of bond numbers, it would appear that valences 5 and 7 can be rejected. This leaves valences 1 and 3, with the former being the least likely to be compatible with all the requirements that must be met. The remaining valence 3 is also a prime and would consequently require a valence 6 for Hg if a model consistent with integral valences and simple ratio division of bond numbers (as well as all of the other requirements) is to be maintained. With these facts in mind, if one now assigns to Ag and Cu the metallic valence 3 and to Hg the metallic valence 6, he finds that it is possible to construct a bound state having the required atomic ratios, as well as the additional features that the structure could be rapidly formed, could be strongly oriented at the electrode surface, and could rotate as the surface charge increases. This is a four-atom species

\[
\begin{align*}
&\text{[Ag}^+\text{]}_{\text{sol}} + \text{[Cu}^{++}\text{]}_{\text{sol}} + 3e^- \rightarrow \text{Ag-Cu} \\
&\text{Ag-Cu} + [\text{Hg-Hg}]_{\text{elect}} \rightarrow \begin{array}{c}
\text{Ag-Cu} \\
\text{Hg-Hg}
\end{array}_{\text{elect}}
\end{align*}
\]

The ring numbers in the preceding diagram represent the fractional bond directed toward each atom, with Cu having 1/3 of a valence bond to Ag and 2/3 of a valence bond to Hg; Hg having 1/3 of a valence bond to Cu and 2/3 of a valence bond to Hg; and so on around the ring. (No attempt is being made to accurately depict bond lengths or angles in these diagrams. Also, the schematics in this appendix should not be interpreted as planar structures. Implicit in this discussion is an additional assumption that if other bound states were present these would be less buoyant than the species being considered. Hence, these would not be electrolyzed onto a bead when the assumed species is present at the electrode surface.) This structure would be expected to have the Cu oriented
upward under normal circumstances (no electrode surface charge), since the mercury end is most similar to the substrate surface. Hence, a preferential intermingling of the mercury end of the structure with substrate surface atoms is consistent with a minimization of energy. However, due to the attraction of the electrons in the bond forming orbitals, the structure may rotate as shown in response to a positive surface charge. It is now hypothesized that the reaction yielding Cu but no Ag or Hg (low voltage) occurs as follows (without changing metallic valences):

\[
\begin{align*}
\text{Outward normal} & \quad \begin{array}{c}
\text{Cu} \\
\text{Ag} \\
\text{Hg}
\end{array} + \begin{array}{c}
\text{Cu} \\
\text{Ag} \\
\text{Hg}
\end{array} \\
\text{Rotation tendency} & \quad \rightarrow
\end{align*}
\]

The bond breaking is viewed as a collision mechanism where rotation brings the Cu parts of two molecules together to form the intermediate Cu$_2$, which then dissociates, oxidizes, and enters solution. (The hypothesized intermediate diatomic Cu$_2$ is known to exist in the gas phase and has a small ground-state dissociation energy of 0.17 electron volt (ref. 17, p. 525).) It is also possible that this reaction (forming Cu$_2$) might occur more slowly as a result of thermal motion at the mercury surface in the absence of a surface charge and, hence, might account for the copper colored film described in table III, entry 7. On the other hand, a probable high-voltage reaction leaving Ag and Hg but no Cu on the bead could be
Here, a larger rotational energy at the high applied voltage now "ejects" Cu$_2$ into the electrode surface, with possible bond formation with electrode mercury to yield a four-membered ring, which, in turn, might dimerize to form an eight-membered ring. In this high-voltage mechanism the two Hg$_2$ diatomics would be ejected up and away from the electrode surface as indicated.

It is conceivable that the double triangular structure postulated as a species left in the electrode in low-voltage stripping could also be a species resulting when Cu is added alone to mercury, and might also be formed with either Ag, Au, or Cu (or a combination of these) when these species have been in mercury for some time. Such structure is an example of a bound state that could release only mercury in anodic stripping, and may account for the fact that only mercury appeared on the bead when copper was added, or when the mercury later found to be contaminated with Ag, Au, and Cu was electrolyzed. The stripping is visualized as a process that lifts the structure from the electrode surface where the two triangles are joined:
The two most strongly bound Hg atoms are brought together by a combination lifting-rotating motion, with the 2/3 bonds being broken in the process, and remade between the bottom mercury atoms. As before, the resulting four-membered ring may dimerize to form an eight-membered structure. The lifting mechanism can be understood by a detailed view of bond straining and vibration, where the lifting motion is viewed as the result of the 2/3 bond breaking:
In this process Hg$_2$ would be violently ejected from the electrode surface in a "slingshot" fashion, and is compatible with the observation of vigorous activity at the electrode surface in high-voltage experiments with no added contaminants (table III, entry 4). The bond breaking motion is considered to be an amplified version of a normal vibrational mode that would occur in the four membered structure:

For a planar structure, the vibrational mode would be as indicated, whereas for a non-planar structure the preceding sketch should be interpreted as a projection of the vibrational motion onto a plane. The existence of ring structures as hypothesized might account for the difficulty in removing Ag, Au, and Cu from mercury completely, even by high-voltage anodic stripping. The only effective means of removing structures as these may well be by scavenging as was accomplished by calcium dispersion.

Finally, it should be mentioned that with regard to the four-membered Ag, Cu, Hg structure, there may be a possibility of modifying the ion exchange bead experiments to form a spectrometer capable of measuring the natural molecular rotation frequency at the electrode surface. Such information could then be used as evidence to verify the correctness of the structure, much the same as one would use ordinary spectral data. It has already been established that the structure in figure 11 will reorient in response to a large enough positive charge at the electrode surface. Thus, there must be some intermediate transition voltage where the appearance of only copper on the bead would give way to the appearance of silver plus mercury on the bead. Suppose now that one operates the experiment at just below this transition voltage, where copper alone appears. If one now couples the direct-current circuit to a radio frequency transmitter (fig. 15), the resulting applied potential will consist of a sinusoidal modulation about the applied direct current potential. If the applied potential resulting from this modulation exceeds the transition voltage for a time equal to or greater than the reciprocal of the natural rotational frequency of the molecular species, a resonance should occur, flipping some of the molecules over. Whereas for time intervals shorter than this critical time only copper would appear on the bead, at resonance a combination of copper, silver, and mercury is likely to appear.
Figure 15. - Schematic of ion exchange bead cell operated as resonance spectrometer in the UHF range. Mercury sample is part of a dipole antenna with a stub support termination. A molecule will respond to the modulation if the effective applied voltage remains above the transition voltage for a time greater than or equal to a critical time $t_c$ required for the molecule to flip over.
REFERENCES


"The aeronautical and space activities of the United States shall be
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