Notes
1. Alternatively, grease and organic materials can be removed by heating platinum electrodes to redness in a flame. Do not touch electrode surfaces with your fingers after cleaning because grease and oil cause nonadherent deposits that can flake off during washing and weighing.
2. Chloride ion must be totally excluded from this determination because it attacks the platinum anode during electrolysis. This reaction not only is destructive but also causes positive errors in the analysis by codepositing platinum with copper on the cathode.
3. If desired, the tin content can be determined gravimetrically by ignition of the SnO$_2 \cdot x$H$_2$O to SnO$_2$.
4. It is important to maintain a potential between the electrodes until they have been removed from the solution and washed. Some copper may redissolve if this precaution is not observed.
5. Experience has shown that a small amount of moisture is retained by the PbO$_2$ and that better results are obtained if 0.8643 is used instead of 0.8662, the stoichiometric factor.

### 37L COULOMETRIC TITRATIONS

In a coulometric titration, the “reagent” is a constant direct current of exactly known magnitude. The time required for this current to oxidize or reduce the analyte quantitatively (directly or indirectly) is measured. See Section 22D-5 for a discussion of this electroanalytical method.

#### 37L-1 The Coulometric Titration of Cyclohexene

**Discussion**

Many olefins react sufficiently rapidly with bromine to permit their direct titration. The reaction is carried out in a largely nonaqueous environment with mercury(II) as a catalyst. A convenient way of performing this titration is to add excess bromide ion to a solution of the sample and to generate the bromine at an anode that is connected to a constant-current source. The electrode processes are

\[
\begin{align*}
2 \text{Br}^- & \rightarrow 2 \text{Br}_2 + 2e^- \quad \text{anode} \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2(g) \quad \text{cathode}
\end{align*}
\]

The hydrogen produced does not react with bromine rapidly enough to interfere. The bromine reacts with an olefin, such as cyclohexene, to give the addition product:

![Addition of bromine to cyclohexene](image)

The amperometric method with twin-polarized electrodes (page 683) provides a convenient way to detect the end point in this titration. A potential difference of 0.2

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12This procedure was described by D. H. Evans in *J. Chem. Educ.*, 1968, 45 (1), 88.
to 0.3 V is maintained between two small electrodes. This potential is not sufficient
to cause the generation of hydrogen at the cathode. Thus, short of the end point, the
cathode is polarized and no current is observed. At the end point, the first excess of
bromine depolarizes the cathode and produces a current. The electrode reactions at
the twin indicator electrodes are

\[
\begin{align*}
2\text{Br}^- & \rightarrow 2\text{Br}_2 + 2e^- \quad \text{anode} \\
\text{Br}_2 + 2e^- & \rightarrow 2\text{Br}^- \quad \text{cathode}
\end{align*}
\]

The current is proportional to the bromine concentration and is readily measured
with a microammeter.

A convenient way to perform several analyses is to initially generate sufficient
bromine in the solvent to give a readily measured current, say 20 \(\mu\)A. An aliquot of
the sample is then introduced, after which the current immediately decreases and
approaches zero. Generation of bromine is again commenced, and the time needed
to regain a current of 20 \(\mu\)A is measured. A second aliquot of the sample is added
to the same solution, and the process is repeated. Several samples can thus be ana-
lyzed without changing the solvent.

The procedure that follows is for the determination of cyclohexene in a
methanol solution. Other olefins can be determined as well.

---

**PREPARATION OF SOLVENT**

Dissolve about 9 g of KBr and 0.5 g of mercury(II) acetate (Note 1) in a mixture
consisting of 300 mL of glacial acetic acid, 130 mL of methanol, and 65 mL of
water (sufficient for about 35 mmol of Br\(_2\).) (Caution! Mercury compounds are
highly toxic, and the solvent is a skin irritant. If inadvertent contact occurs, flood
the affected area with copious quantities of water.)

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**PROCEDURE**

Obtain the unknown in a 100-mL volumetric flask; dilute to the mark with
methanol, and mix well. The temperature of the methanol should be between 18°C
and 20°C (Note 2).

Add sufficient acetic acid/methanol solvent to cover the indicator and generator
electrodes in the electrolysis vessel. Apply about 0.2 V to the indicator electrodes.
Activate the generator electrode system, and generate bromine until a current of
about 20 \(\mu\)A is indicated on the microammeter. Stop the generation of bromine,
record the indicator current to the nearest 0.1 \(\mu\)A, and set the timer to zero.
Transfer 10.00 mL of the unknown to the solvent; the indicator current should
decrease to almost zero. Resume bromine generation. Produce bromine in smaller
and smaller increments by activating the generator for shorter and shorter periods
as the indicator current rises and approaches the previously recorded value. Read
and record the time needed to reach the original indicator current. Reset the timer
to zero, introduce a second aliquot of sample (make the volume larger if the time
needed for the first titration was too short, and conversely), and repeat the process.
Titrate several aliquots.

Report the mass in milligrams of cyclohexene in the unknown.
Notes
1. Mercury(II) ions catalyze the addition of bromine to olefinic double bonds.
2. The coefficient of expansion for methanol is 0.11%/°C; thus, significant volumetric errors result if the temperature is not controlled.

**37M VOLTAMMETRY**

Various aspects of polarographic and amperometric methods are considered in Chapter 23. Two examples that illustrate these methods are described in this section. Enormous diversity exists in the instrumentation available for these determinations. It will thus be necessary for you to consult the manufacturer’s operating instructions concerning the details of operation for the particular instrument you will use.

**37M-1 The Polarographic Determination of Copper and Zinc in Brass**

**Discussion**

The percentage of copper and zinc in a sample of brass can be determined from polarographic measurements. The method is particularly useful for rapid, routine analyses; in return for speed, however, the accuracy is considerably lower than that obtained with volumetric or gravimetric methods.

The sample is dissolved in a minimum amount of nitric acid. It is not necessary to remove the SnO_{2} \cdot xH_{2}O produced. Addition of an ammonia/ammonium chloride buffer causes the precipitation of lead as a basic oxide. A polarogram of the supernatant liquid has two copper waves. The one at about −0.2 V (versus SCE) corresponds to the reduction of copper(II) to copper(I), and the one at about −0.5 V represents further reduction to the metal. The analysis is based on the total diffusion current of the two waves. The zinc concentration is determined from its wave at −1.3 V. For instruments that permit current offset, the copper waves are measured at the highest feasible sensitivity. These waves are then suppressed by the offset control of the instrument, and the zinc wave is obtained, again at the highest possible sensitivity setting.

**PREPARATION OF SOLUTIONS**

1. *Copper(II) solution*, 2.5 × 10^{-2} M. Weigh (to the nearest milligram) 0.4 g of copper wire. Dissolve in 5 mL of concentrated HNO_{3} (use the hood). Boil briefly to remove oxides of nitrogen; then cool, dilute with water, transfer quantitatively to a 250-mL volumetric flask, dilute to the mark with water, and mix thoroughly.
2. *Zinc(II) solution*, 2.5 × 10^{-2} M. Dry reagent-grade ZnO for 1 hr at 110°C, cool in a desiccator, and weigh 0.5 g (to the nearest milligram) into a small beaker. Dissolve in a mixture of 25 mL of water and 5 mL of concentrated HNO_{3}. Transfer to a 250-mL volumetric flask, and dilute to the mark with water.
3. *Gelatin*, 0.1%. Add about 0.1 g of gelatin to 100 mL of boiling water.
4. *Ammonia/ammonium chloride buffer* (sufficient for about 15 polarograms). Mix 27 g of NH_{4}Cl and 35 mL of concentrated ammonia in sufficient distilled water to give about 500 mL. This solution is about 1 M in NH_{3} and 1 M in NH_{4}^{+}.