

PLATINUM IN CHLOROPLATINIC ACID BY SPECTROPHOTOMETRY

UOP Method 876-93

SCOPE

This method is for determining platinum by non-differential spectrophotometry in chloroplatinic acid (CPA) solutions that are homogeneous and free of precipitate. Platinum concentrations in the range of 20 to 30 mass-% are typically determined, but the method is not limited to this range. Platinum cannot be determined in the presence of rhenium, iridium and rhodium, which produce colored ions during the color development step and will cause a positive error. However, these elements are not expected to be present in quantities that interfere after the dilution step specified in this method.

OUTLINE OF METHOD

Triplicate samples of CPA solutions are weighed into volumetric flasks and diluted by mass with hydrochloric acid. A weighed portion of the dilute CPA solution is treated with additional hydrochloric acid and hydrogen peroxide. A hydrochloric acid solution of stannous chloride is added to the treated platinum solution and a spectrophotometric measurement of the yellow color produced is made at 403 nm.

The concentration of the dilute platinum solution is determined by comparing the platinum absorbance to a standard calibration curve prepared from standard platinum solutions. The platinum content is then calculated based on the platinum concentration in the dilute solution and the dilution factor.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, electronic, readability 0.1-mg

Balance, electronic, top-loading, readability 0.01-g

Beaker, Berzelius, tall form, 300-mL, calibrated 25- to 250-mL, with spout, borosilicate glass, Fisher Scientific, Cat. No. 02-546C. Each beaker must be marked with an identification number.

Beaker, borosilicate glass, 400-mL, Fisher Scientific, Cat. No. 02-540L

Bottle, narrow mouth, round, amber glass, 237-mL, with molded plastic conical polyethylenelined cap, Fisher Scientific, Cat. No. 03-320-6C

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Bottle, washing, polyethylene, 500-mL, Fisher Scientific, Cat. No. 03-409-10E

Buret, weighing, 10-mL, Kimble Science Products, Cat. No. 17200F-10

Calculator, or computer, capable of least squares analysis

Cells, spectrophotometric, 10-mm path length, near-UV glass, rectangular, sold as a set of two matched, although only one is required, Fisher Scientific, Cat. No. 14-385-910A. Alternatively, a stationary flow cell may be used (see Note 1).

Cylinders, graduated, plastic, polymethylpentene (PMP), 10-, 25-, 50-, 100-, and 500-mL, Fisher Scientific Cat Nos. 08-572-5A, B, C, D and F, respectively

Flasks, Kjeldahl, 100-mL, Fisher Scientific, Cat. No. 10-110C

Flasks, volumetric, Class A, 50-, 100-, 250- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5B, C, E and G, respectively

Funnels, filter, 58 degree angle bowl, short stem, 55- and 100-mm diameter, Fisher Scientific, Cat. Nos. 10-322C and 10-322G, respectively

Glass beads, 3-mm, solid, borosilicate, Kimble Scientific Products, Cat. No. 13500-3. Rinse with water to remove glass chips and allow to dry before use. Alternatively, use of a small magnetic stirring bar is preferred for preparation of the platinum standard.

Hot plate-stirrer, remote control, adjustable heat and stirrer, ceramic top, heating range 65 to 510°C, Fisher Scientific, Cat. No. 11-495-59A

Pipets, Mohr, 1-, 5-, 10- and 25-mL, Fisher Scientific, Cat. Nos. 13-665F, K, M and N, respectively

Pipet, Pasteur, borosilicate glass, Fisher Scientific, Cat No. 13-678-20C

Spectrophotometer, minimum absorbance repeatability of ± 0.0003 at 0.1 Abs, noise less than 0.00005 Abs (rms) at 0.0 Abs, and 0.0006 Abs (rms) at 2.0 Abs, minimum stability of 0.0003 Abs per hour, readability to 0.0001 Abs, Varian Instrument Group, Cary Model 4 (Note 2)

Standards, absorbance, spectrophotometric, certified, glass filters, 10-30% transmittance, 440- to 635-nm wavelength range, National Institute of Standards and Technology (NIST), Cat. No. SRM-930-D

Stirring bars, Teflon coated, 3.2 by 13-mm ($1/8 \times 1/2$ -in.) and 9.5 by 25-mm ($3/8 \times 1$ -in.), Fisher Scientific, Cat. Nos. 14-511-61 and 09-311-9, respectively

Watch glass, ribbed, borosilicate glass, 75-mm diameter, Fisher Scientific, Cat. No. 02-613A

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water, except where noted.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Filter paper, Whatman No. 50, quantitative, hardened, low ash, 185-mm diameter, Fisher Scientific, Cat. No. 09-865G

Glass wool, borosilicate glass, Fisher Scientific, Cat. No. 11-388

Hydrochloric acid, concentrated, 37%

Hydrochloric acid, 1:1. Dilute 500 mL of concentrated hydrochloric acid measured with a graduated cylinder with an equal volume of water. Add the acid to the water and mix.

Hydrogen peroxide, 30%

Lens paper, optical, Fisher Scientific, Cat. No. 11-996

Nitric acid, concentrated, 70%

Platinum wire, 99.998% minimum purity, Puratronic, 0.25-mm OD, Aesar, Cat. No. 10958

Stannous chloride, dihydrate, Baker Analyzed Reagent Grade, lot analysis provided, 99.9% minimum purity, J.T. Baker Chemical, Cat. No. 3980 (see Note 3)

Stannous chloride solution. In a beaker while stirring, dissolve 50 ± 0.01 g of the stannous chloride in 50 mL of concentrated hydrochloric acid with gentle warming if necessary. Quantitatively transfer the solution to a 100-mL volumetric flask and dilute to approximately 95 mL with water. Allow to cool to ambient temperature, dilute to the mark with water and mix by inverting several times. Filter the solution through a fluted Whatman No. 50 filter paper into a second 100-mL volumetric flask. This solution must be prepared daily.

Test paper, potassium iodide-starch, Fisher Scientific, Cat. No. 14-860

PROCEDURE

To avoid errors introduced by weighing volumetric flasks with stoppers that can be mismatched to another flask in a subsequent weighing step, it is recommended that all weighings of volumetric flasks, from initial taring to weighing of the final solution volume, be performed without stoppers in place. This proviso is applicable to all sections of this method involving weighing of volumetric flasks.

All subsequent steps involving handling and heating of concentrated acids or acid solutions must be performed in a fume hood.

Preparation of Standard Platinum Solution

Prepare a standard platinum solution containing 1.0 mg platinum/g as follows:

1. Weigh 1.0 g of 99.998% platinum wire to the nearest 0.1 mg.
2. Transfer the platinum wire quantitatively into a 100-mL Kjeldahl flask. Place the flask in a 400-mL beaker. Add either glass beads or, preferably, a small magnetic stirring bar.
3. Add 10 mL of concentrated nitric acid and 25-mL of concentrated hydrochloric acid.
 - Treatment of the platinum is conducted at ambient temperature until evolution of chlorine has subsided.
4. Place the solution on a stirrer hot plate and heat to a gentle boil.
 - Stirring slowly with a magnetic stir bar prevents bumping.
5. Maintain the solution volume at approximately 30 mL by the dropwise addition of concentrated nitric and hydrochloric acids in a ratio of 1 to 3, until the platinum wire dissolves.

- When adding the acids, take care that no solution is lost by spattering.
6. Evaporate the acid solution slowly to a syrup, approximately 3 mL, by gently boiling.
 - It is imperative that the solution does not go to dryness during the volume reduction. Platinum losses will result.
 7. Add 1 to 2 mL of concentrated hydrochloric acid, slowly with a Pasteur pipet, and then add 1 to 2 mL of hydrogen peroxide, dropwise with a Pasteur pipet, to the evaporating solution and boil gently. Repeat the addition and boil until evolution of the brown nitrogen dioxide fumes ceases.
 8. Add 10 mL of concentrated hydrochloric acid and 50 mL of water to the solution.
 9. Remove the flask from the hot plate and allow the platinum solution to cool to ambient temperature.
 10. Transfer the platinum solution quantitatively to a one-liter volumetric flask, tared to the nearest 0.01 g.
 11. Add 15 mL of concentrated hydrochloric acid to the solution.
 12. Dilute with water to a mass that produces a platinum concentration as close as possible to 1.0000-mg platinum per gram of solution, weighed to the nearest 0.01 g.
 - Calculate the Pt concentration on a mass basis by dividing the mass of Pt in mg by the net solution mass in grams for use in Equation 2. For example, if 1.0034 g of platinum wire was dissolved, and the final mass of the platinum solution was 1003.21 g, the Pt concentration would be 1.0002 mg Pt/g.
 13. Cap and mix the solution thoroughly by shaking and inverting the flask at least 10 times.
 14. Subdivide the standard platinum solution, without dilution, into separate 237-mL (or smaller), amber glass bottles and seal with polyethylene lined caps for storage.
 - The stability of the solution in an unopened bottle is not known.
 - Once opened, the standards cannot be used for more than four weeks.

Determination of Sample Mass

1. Determine the relative density of the CPA solution, as received, by ASTM D 4052 or any other acceptable technique.
 - If an estimate of the platinum concentration is already known, the relative density does not need to be determined and work can begin at Step 3.
2. Estimate the platinum concentration using the relative densities listed in Table 1.
3. Determine the sample mass for analysis from Table 2 using the estimated platinum concentration.

Preparation of Samples and Standards for Analysis

1. Transfer from a tared weighing buret three portions of the CPA sample, weighed to the nearest 0.1 mg, into individual, dry 250-mL volumetric flasks, weighed to the nearest 0.01 g. Record the masses taken.
 - Table 2 shows the appropriate sample mass to be used.
 - The sample mass will be read as a minus value on the balance.
2. Add 25 mL of concentrated hydrochloric acid to each volumetric flask.

3. Dilute each sample with water to the mark, weigh to the nearest 0.01 g, stopper and thoroughly mix by inverting several times.

Table 1

**Platinum Content of CPA Solutions at 24°C at
Various Relative Densities**

Relative Density @ 24°C	Estimated Platinum Content of CPA, mass-%
1.38	18
1.45	20
1.51	22
1.58	24
1.66	26
1.75	28
1.85	30
1.99	32

Table 2

**Approximate Sample and Aliquot Mass for Color Development at
Various Platinum Concentrations**

Est. Pt Content of CPA, mass-%	Sample Mass For Analysis, g	Aliquot, g	mg Pt/100 mL	Normal Abs
17.5	2.24	1.0	1.6	0.63
20.0	2.05	1.0	1.6	0.63
22.5	1.75	1.0	1.58	0.63
25.0	1.5	1.0	1.5	0.60
27.5	1.5	1.0	1.65	0.66
30.0	1.25	1.0	1.5	0.60
32.5	1.25	1.0	1.63	0.65

4. Transfer a one-gram aliquot of each sample solution, weighed to the nearest 0.1 mg, into a weighed 300-mL tall-form beaker with a Pasteur pipet.
 - The weighing must be performed rapidly because of possible evaporation.
 - A separate Pasteur pipet is to be used for each sample solution.
5. Transfer, from a tared weighing buret, weighed to the nearest 0.1 mg, 0.8-, 1.2-, 1.6- and 2.0-g of platinum standard into four separate 300-mL beakers, respectively. Record the masses taken. Reserve a fifth beaker as a blank.
 - The platinum contents must span the platinum content expected in the sample.
 - The standard mass taken will be read as a minus value on the balance.

6. Add three glass beads or preferably a magnetic stir bar to the samples, standards and blank (see Note 4).
7. Add 40 mL of concentrated hydrochloric acid and 3 mL of hydrogen peroxide to the samples, standards and blank.
8. Cover each beaker with a ribbed watch glass and allow them to stand for 5-10 minutes.
9. Place the beakers on a stirrer-hot plate and bring to a boil, while gently stirring.
10. Reduce the volume to approximately 25 mL and maintain this volume by periodic additions of concentrated hydrochloric acid. Boil the samples, standards and blank until all chlorine is removed, approximately 30 minutes.
 - The headspace above the boiling sample is checked with potassium iodide-starch test strips premoistened with water before use. The color of the test strip remains white when all chlorine has been removed.
11. Remove the samples, standards and blank from the hot plate and allow them to cool.

Color Development and Absorbance Measurement

1. Transfer the blank, standards and samples quantitatively to dry, pre-weighed (to the nearest 0.01 g) 100-mL volumetric flasks with 1:1 hydrochloric acid.
 - The glass boiling beads are removed by passing the solution through a very small pad of glass wool inserted into the stem of the funnel used to transfer the solutions to the volumetric flask. If a magnetic stirring bar is used, it is held back with a second magnet outside the beaker.
2. Dilute to approximately 80 mL with 1:1 hydrochloric acid and swirl to mix.
3. Add 8 mL of stannous chloride solution to the blank, standards and samples, using a Mohr pipet and swirl to mix.
4. Rinse down the neck of the flask and dilute to a volume of approximately 95 mL with 1:1 hydrochloric acid, swirl to mix, then stopper the flask.
 - Do not wet the stopper by inverting the flask.
5. Allow the color of the blank, standards and samples to develop at the same temperature for 1-1/2 hours.
6. Dilute the blank, standards and samples to the mark with 1:1 hydrochloric acid, reweigh the flasks (to the nearest 0.01 g), then stopper and thoroughly mix the solutions by inverting the volumetric flasks several times.
7. Calibrate the spectrophotometer once a week at a wavelength of 440 nm with the certified NIST glass filter absorbance standard as outlined in the instrument manual.
 - Spectrophotometers that utilize internal calibration cannot be calibrated with an external standard. In this case the NIST standard can be used as a performance check.
 - The certified solid standards must be periodically recertified.
8. Adjust the spectrophotometer using the specific instructions supplied by the manufacturer.
9. Zero the spectrophotometer with water in a 10-mm cell on the sample side and air, without a cell, in the reference side.

- If a flow cell is used, see Note 1.
10. Read the absorbance of the blank, and each standard and sample solution, to four decimal places using a 10-mm cell at a wavelength of 403 nm (Notes 1 and 2).
 - The absorbance of all the solutions must be measured within one hour after color development is completed and the temperature of all solutions must be the same within one degree C.
 - The absorbance must be determined within one minute after the cell has been placed in the spectrophotometer unless the cell compartment is thermostatically controlled.
 11. Check the spectrophotometer zero to verify that the values are constant within the precision of the instrument.
 - If the zero is not constant (± 0.001 for a 3-place instrument or ± 0.0003 for a 4-place instrument), repeat Steps 9 through 11.
 12. Calculate the blank corrected platinum absorbance (A) of the standards and samples using the following equation:

$$A = B - C \quad (1)$$

where:

A = blank corrected absorbance of platinum in standard or sample
B = uncorrected absorbance of standard or sample
C = absorbance of blank

CALCULATIONS

Spectrophotometer Response

Calculate the concentrations of platinum in the color developed Pt standards to five significant figures as follows:

$$D = \frac{EF}{G} \quad (2)$$

where:

D = concentration of platinum in the color developed platinum standard, mg/g
E = mass of platinum standard taken, g
F = concentration of platinum standard solution, mg/g
G = total mass of color developed standard solution, g

Calculate the best straight line from the four net absorbances (Eq. 1) and the corresponding concentrations of the platinum standards in mg/g by performing a least squares analysis and obtain the correlation coefficient (Q) to 8 decimal places. Use a calculator capable of least squares analysis or the data reduction system on the spectrophotometer, if available. If the correlation coefficient (Q) is less than 0.99986, one suspect standard may be safely discarded and the best straight line recomputed to obtain a correlation coefficient of 0.99986 or larger. In no case can a two-point calibration, obtained by using the “best” two of the standards, be used.

Platinum in CPA

Calculate the platinum concentration of the color developed sample solutions (I), in mg/g, by using the computation algorithm of the calculator or computer used to calculate the best straight line and entering the net absorbance of the sample.

Calculate the platinum concentration of the original CPA solutions to the nearest 0.001 mass-% as follows:

$$\text{Pt, mass-\%} = \frac{IMK}{10 LH} \quad (3)$$

where:

- H** = mass of CPA taken for analysis, g
- I** = platinum concentration of the color developed sample solution, mg/g
- K** = mass of diluted CPA, g
- L** = mass of diluted CPA taken for analysis, g
- M** = mass of color developed solution, g
- 10** = required to convert to mass-%

Calculate and report the platinum concentration of the CPA sample to four significant figures by averaging the 3 determinations (Note 5).

NOTES AND PRECAUTIONS

1. The same cell must be inserted in the same way in the light beam each time a measurement is made using air as a reference. Alternatively, a flow-through sample cell, which is never removed from the spectrophotometer, might be used providing conditions are arranged to ensure complete removal of the previous sample each time spectrophotometric data are measured. Proper use of a flow-through cell requires thorough clean-out between blanks, standards and samples. The cell must first be flushed five times with a 1:1 mixture of concentrated hydrochloric acid and methanol, followed by five rinses with water. The instrument is then zeroed with water in the sample cell, versus air. Then flush the cell five times with 1:1 hydrochloric acid/water. Follow this with five flushes (to a constant optical density reading) for the blank and then for each of the standards and samples using the next standard or sample solution to rinse out the previous one from the flow cell. After the last sample has been measured, flush the cell with five flushes of 1:1 hydrochloric acid/water, followed by five flushes with water, ending with a recheck of the instrument zero at 403 nm.

2. If the spectrophotometer does not fulfill *all* of the specifications, then a spectrophotometer capable of accurate and precise measurement of the absorbance to 3-decimal places (i.e., 0.001 Abs), may be used. But, each absorbance *must* be determined a minimum of 9 times. The nine absorbance readings are then averaged to obtain the absorbance that would be equivalent to that read with a 4-decimal place instrument.

3. Oxidation or hydrolysis of the stannous chloride renders the reagent unusable. The reagent must not be used if it has any yellow color, does not dissolve easily in concentrated hydrochloric acid or has remained more than 6 months in an opened bottle.

4. It is recommended that analyses of samples and standards be completed within a single day. If necessary, the analysis may be stopped at this point before the final oxidation step is started (Steps 7 to 11, *Preparation of Samples and Standards for Analysis*). Store the samples in the beaker covered with a watch glass.

5. If the mean of the two closest Pt values differs from the third value by more than the allowable difference established in the laboratory, the third value must be discarded.

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests per lab) and using data collected from each of 4 laboratories, the within-laboratory estimated standard deviations (esd) were calculated for platinum at the concentrations listed in Table 3. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable differences shown in Table 3 at the concentrations listed (95% probability).

Reproducibility

Two tests performed in different laboratories by different analysts, on different days should not differ by more than the allowable differences shown in Table 3 at the concentrations listed (95% probability).

Table 3

Platinum Concentration, mass-%	Repeatability		Reproducibility	
	Within-Lab esd, mass-%	Allowable Difference, mass-%	Between-Lab esd, mass-%	Allowable Difference, mass-%
25.08 (Sponge)	0.065	0.19	0.080	0.36
25.40 (Recycle)	0.064	0.19	0.069	0.31

TIME FOR ANALYSIS

The elapsed time for one analysis is 8 hours. The labor requirement is 6 hours.

REFERENCE

ASTM Method D 4052, 1993 www.astm.org

SUGGESTED SUPPLIERS

Aesar/Johnson Matthey, P.O. Box 1087, Seabrook, NH 03874-1087 (508-521-6300)
 J.T. Baker, Inc., 222 Red School La., Phillipsburg, NJ 08865 (908-859-2151)
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
 Kimble Science Products, Crystal Ave., Vineland, NJ 08360 (609-794-5560)
 National Institute of Standards and Technology (NIST), Office of Standard Reference Materials,
 Gaithersburg, MD 20899 (301-975-6776)
 Varian Instrument Group, 220 Humboldt Ct., Sunnyvale, CA 94089 (408-734-5370)