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Aviation turbine fuels – Determination of mercaptan sulphur – Amperometric and potentiometric methods

Carburants aviation pour turbines – Dosage du soufre sous forme de mercaptans – Méthodes ampérométrique et potentiométrique

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3012 was drawn up by Technical Committee ISO/TC 28, *Petroleum products*, and circulated to the Member Bodies in March 1973.

It has been approved by the Member Bodies of the following countries :

Australia	India	South Africa, Rep. of
Belgium	Iran	Spain
Brazil	Israel	Sweden
Bulgaria	Mexico	Thailand
Canada	Netherlands	Turkey
Chile	New Zealand	United Kingdom
Czechoslovakia	Norway	U.S.A.
France	Poland	U.S.S.R.
Germany	Portugal	
Hungary	Romania	

No Member Body expressed disapproval of the document.

Aviation turbine fuels – Determination of mercaptan sulphur – Amperometric and potentiometric methods

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies two methods for the determination of mercaptan sulphur in aviation turbine fuels containing from 0,000 3 to 0,01 % (*m/m*) of mercaptan sulphur. Organic sulphur compounds such as sulphides, disulphides, and thiophene do not interfere. Elemental sulphur in amounts less than 0,000 5 % (*m/m*) does not interfere. Hydrogen sulphide will interfere, if not removed as described in 3.4.1.

2 PRINCIPLE

2.1 The sample is washed with an aqueous solution of acid cadmium sulphate to remove hydrogen sulphide. The determination of mercaptan sulphur in the hydrogen sulphide-free sample is finished either amperometrically or potentiometrically.

2.2 Using the amperometric finish, the hydrogen sulphide-free sample is dissolved in titration solvent and is titrated amperometrically with silver nitrate standard solution, using a rotating platinum wire indicator electrode and a calomel reference electrode. The diffusion current is measured and plotted against the volume of silver nitrate added. The volume of silver nitrate equivalent to the mercaptan sulphur is determined from the titration curve.

2.3 Using the potentiometric finish, the hydrogen sulphide free sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate standard alcoholic solution, using as an indicator the potential between a glass reference electrode and a silver/silver sulphide indicating electrode. Under these conditions the mercaptan sulphur is precipitated as silver mercaptide and the end point of the titration is shown by a large change in cell potential.

3 AMPEROMETRIC METHOD

3.1 REAGENTS

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to recognized standards for reagent chemicals.

Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equivalent purity.

3.1.1 Acetone

3.1.2 Sulphuric acid (1 + 5).

Carefully add 1 volume of concentrated sulphuric acid (H_2SO_4 , ρ 1,84 g/ml) to 5 volumes of water.

3.1.3 Supporting electrolyte

Dissolve 20 g of ammonium nitrate (NH_4NO_3) in 100 ml of concentrated ammonium hydroxide (NH_4OH , ρ 0,90 g/ml).

3.1.4 Cadmium sulphate, acid solution (150 g/l).

Dissolve 150 g of cadmium sulphate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) in water. Add 10 ml of sulphuric acid (3.1.2) and dilute to 1 l with water.

3.1.5 Potassium chloride, saturated solution.

Prepare a saturated solution of potassium chloride (KCl) in water.

3.1.6 Silver nitrate, 0,100 0 N standard solution.

Dissolve 16,989 g of dry (1 h at 110 °C) silver nitrate (AgNO_3) in water and dilute to 1 l with water in a volumetric flask.

3.1.7 Silver nitrate, 0,010 0 N standard solution.

Dilute 100 ml of the silver nitrate standard solution (3.1.6) to 1 l with water in a volumetric flask.

3.2 APPARATUS

Typical apparatus may be assembled as shown in figure 1, using soldered connections wherever practicable in the electrical circuit.

3.2.1 Burette, capacity 25 ml, graduated in 0,1 ml divisions.

NOTE – Burettes of 25 ml capacity conforming to the requirements of ISO/R 385 – Class B are suitable.

3.2.2 Calomel electrode, sleeve type pencil electrode, either conventional or double junction type.

3.2.3 Electrical circuit as shown in figure 1.

3.2.4 Microammeter, d.c. type having a range from 0 to $30 \mu\text{A}$, a sensitivity of $0,2 \mu\text{A}$ per division, and an internal resistance of 150 to 500Ω .

3.2.5 Rotating electrode, constructed as follows :

Seal a platinum wire 0,5 to 1,0 mm in diameter and 6 to 8 mm long into the end of soft glass tube, 6 mm outside diameter, that has been shaped into a stirrer blade. Place a few drops of mercury in the glass tube, and make electrical contact between the mercury and the chuck of the stirring motor with a piece of copper wire.

Alternatively, a stationary platinum electrode may be used provided the solution is stirred at a constant speed.

3.2.6 Stirrer, that can maintain a constant speed in the range from 500 to 1 000 rev/min. The stirrer may be so constructed that an electrical connection can be made between the rotating electrode and the potential divider.

3.2.7 Voltmeter, d.c. type having a range of 0 to 1 V with a sensitivity of 0,01 V per division.

3.3 PREPARATION OF APPARATUS

3.3.1 Remove the rubber stopper from the side opening of the calomel electrode (3.2.2), or lower the rubber sleeve, and lower the glass sleeve for a few seconds to allow the potassium chloride electrolyte to wet the ground glass joint.

3.3.2 Place 100 ml of acetone (3.1.1) and 5 ml of the supporting electrolyte solution (3.1.3) in a 300 ml tall-form beaker. Place the beaker on the titrating stand and adjust its position so that the tips of the electrodes are at least 25 mm below the surface of the liquid. Start the rotating electrode stirring motor and adjust its speed so that it is

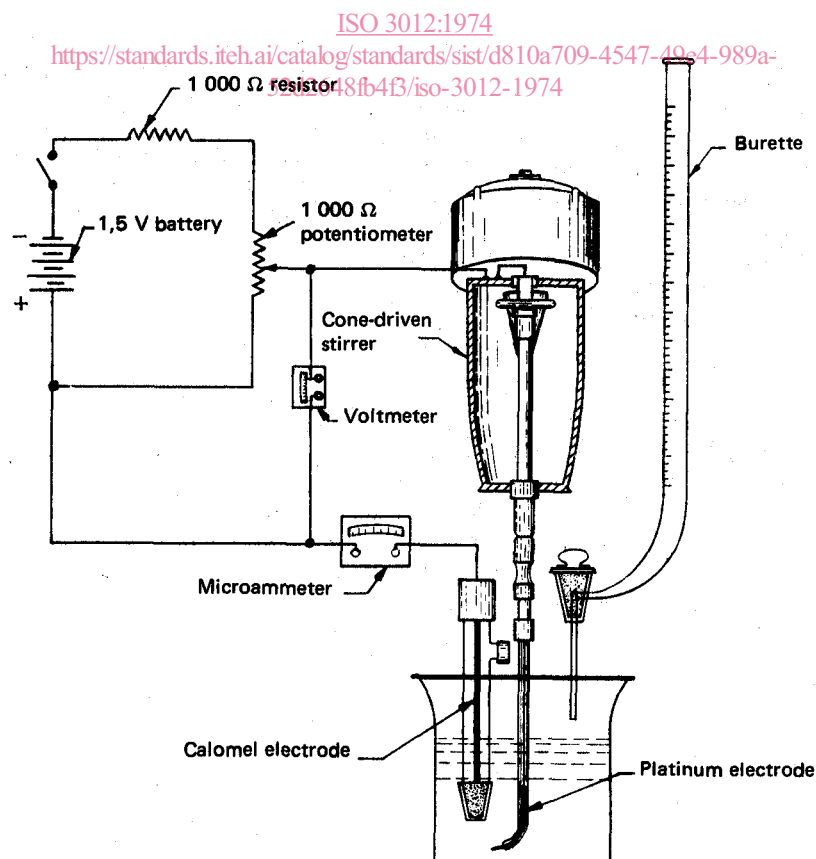


FIGURE 1 – Diagram of amperometric titration apparatus

within the range of 500 to 1 000 rev/min. During a titration this speed must be maintained constant. Close the electrical circuit (3.2.3) and adjust the potential divider, so that $-0,25 \pm 0,02$ V is applied to the platinum electrode, as indicated by the voltmeter (3.2.7). Once the correct voltage has been obtained, do not change the setting of the potential divider during a determination.

3.3.3 Check the apparatus by making a trial titration as follows: Record the microammeter reading (see note). Add 0,10 ml of silver nitrate standard solution (3.1.7) and record the burette and microammeter readings. Continue in this manner, adding small increments of silver nitrate standard solution until a total of 1,00 ml has been added. Plot, on linear graph paper, the quantity in millilitres of silver nitrate standard solution used against the corresponding reading in microamperes. Draw a straight line through the plotted points. The intersection of this line with a horizontal line drawn through the microammeter reading at 0 ml of silver nitrate standard solution indicates the volume of silver nitrate standard solution used to reach the end point. This volume should be less than 0,05 ml of silver nitrate standard solution. If most of the points fall on a reasonably straight line, consider the apparatus to be in satisfactory working condition.

NOTE — The current may increase to 20 or 30 μ A at first, but it will decrease to zero or slightly above in a few minutes.

3.4 PROCEDURE

3.4.1 Removal of hydrogen sulphide

Test the sample qualitatively for hydrogen sulphide (H₂S) by shaking 5 ml of the sample with 5 ml of the cadmium sulphate acid solution (3.1.4). If no precipitate appears, proceed with the analysis of the sample as described in 3.4.2. If a yellow precipitate appears, remove the hydrogen sulphide in the following manner: Place a quantity of the sample, three to four times that required for the analysis, in a separating funnel containing a volume of the cadmium sulphate acid solution equal to one half that of the sample and shake vigorously. Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with another portion of the cadmium sulphate acid solution. Again draw off the aqueous phase, and wash the sample with three 25 to 30 ml portions of water, withdrawing the water after each washing. Filter the hydrocarbon through a rapid filter paper. Test a small portion of the washed sample in a test tube with a few millilitres of the cadmium sulphate acid solution. If no further precipitate is formed, proceed as directed in 3.4.2. If a precipitate appears, repeat the extraction with the cadmium sulphate acid solution until all the hydrogen sulphide has been removed.

3.4.2 Analysis of sample

Measure with a pipette (see note 1), or weigh, 20 to 50 ml of the original or hydrogen sulphide-free sample prepared as described in 3.4.1 into a 300 ml tall-form beaker containing

100 ml of acetone and 5 ml of the supporting electrolyte (see note). Place the beaker on the titration stand, start the stirring motor, and close the electrical circuit. Begin the titration by adding small increments of the silver nitrate standard solution (3.1.7). Record the microammeter and burette readings after each addition. The end point region is indicated by a rapid increase in the microammeter readings. When the microammeter indicates that the end point has been passed, add four or five small increments of silver nitrate standard solution, recording the microammeter and burette readings after each addition. Plot the cumulative volume of silver nitrate standard solution used against the corresponding readings in microamperes on linear graph paper. Draw a straight line through the increasing current readings and a horizontal line through the minimum current readings (see figure 2). The point of intersection of the two lines indicates the volume of silver nitrate standard solution that is equivalent to the mercaptan sulphur content of the sample.

NOTES

1 If the test portion is measured volumetrically, the density shall be determined by a suitable method capable of reproducing results to within 0,001 5 g/ml.

2 A larger amount of acetone may be used if it is required to dissolve the sample.

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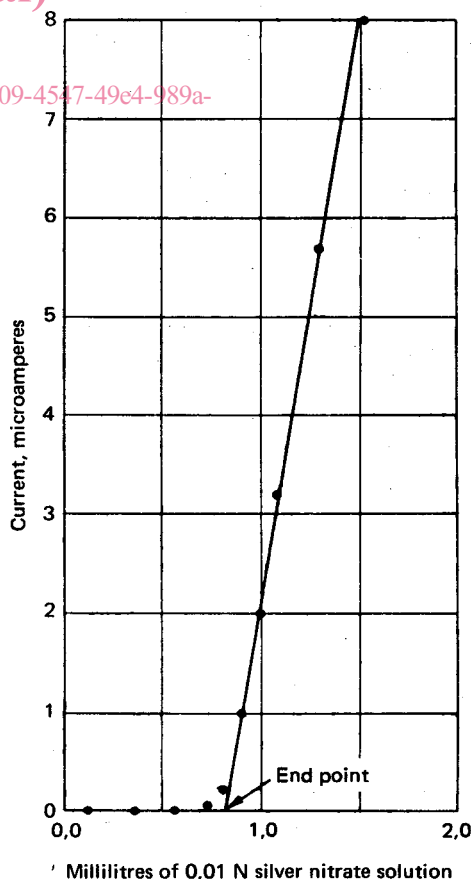


FIGURE 2 — Typical amperometric titration curve for liquid hydrocarbon samples

3.5 CALCULATION

The mercaptan sulphur content, as a percentage by mass, of the sample is given by the formula

$$3,206 \frac{VT}{m}$$

where

V is the volume, in millilitres, of silver nitrate solution required;

T is the normality of the silver nitrate solution;

m is the mass, in grams, of the test portion.

3.6 PRECISION

The following criteria shall be used for judging the acceptability of results (95 % confidence level).

3.6.1 Duplicate results by the same operator shall be considered suspect if they differ by more than the following amounts :

Mercaptan sulphur content % (m/m)	Repeatability
0,000 3 to 0,001	0,000 1
0,001 to 0,005	0,000 2
0,005 to 0,010	0,000 5

3.6.2 The results submitted by each of two laboratories shall be considered suspect if the two results differ by more than the following amounts :

Mercaptan sulphur content % (m/m)	Reproducibility
0,000 3 to 0,001	0,000 4
0,001 to 0,005	0,000 6
0,005 to 0,010	0,000 9

4 POTENTIOMETRIC METHOD

4.1 REAGENTS¹⁾

4.1.1 Cadmium sulphate, acid solution (150 g/l).

See 3.1.4.

4.1.2 Sodium sulphide solution (10 g/l).

Dissolve 10 g of sodium sulphide (Na₂S) in water and dilute to 1 l with water. Prepare a fresh solution as needed.

4.1.3 Titration solvent.

Dissolve 2,7 g of sodium acetate trihydrate (NaC₂H₃O₂·3H₂O), or 1,6 g of anhydrous sodium acetate (NaC₂H₃O₂) in 20 ml of oxygen-free water, pour into 975 ml of *isopropyl* alcohol (99 %) (see note to 4.1.6) and add 4,6 ml of glacial acetic acid. To remove dissolved oxygen purge the solution with a rapid stream of nitrogen for 10 to 15 min each day prior to use; keep protected from the atmosphere.

4.1.4 Potassium iodide, 0,1 N standard solution.

Dissolve approximately 17 g of potassium iodide (KI), weighed to the nearest 0,01 g, in water and dilute to 1 l in a volumetric flask with water. Calculate the exact normality.

4.1.5 Silver nitrate, 0,1 N standard alcoholic solution.

Dissolve 17 g of silver nitrate (AgNO₃) in 100 ml of water and dilute to 1 l with *isopropyl* alcohol (99 %) (see note to 4.1.6), store in a dark bottle and standardize weekly.

To standardize, add 6 drops of concentrated nitric acid (HNO₃, ρ 1,42 g/ml) to 100 ml of water in a 300 ml tall-form beaker, and remove the oxides of nitrogen by boiling for 5 min. Cool, pipette 5 ml of the potassium iodide solution (4.1.4) into the beaker, and titrate with the silver nitrate solution, choosing the end point at the inflection of the titration curve.

4.1.6 Silver nitrate, 0,01 N standard alcoholic solution.

Prepare daily by dilution of 100 ml of silver nitrate alcoholic solution (4.1.5) to 1 l with *isopropyl* alcohol (99 %) in a volumetric flask. Calculate the exact normality.

NOTE — It is important to pass the *isopropyl* alcohol through a column of activated alumina to remove peroxides that may have formed on storage; failure to remove peroxides will lead to low results.

4.2 APPARATUS

4.2.1 Burette, capacity 10 ml, graduated in 0,05 ml intervals, with a tip that extends approximately 120 mm below the stopcock.

NOTE — Burettes of 10 ml capacity conforming to the requirements of ISO/R 385 — Class B are suitable.

1) For purity of reagents, see 3.1.

4.2.2 Cell system, consisting of a reference and an indicating electrode.

The reference electrode shall be a sturdy, pencil-type glass electrode, having a shielded lead connected to ground. The indicating electrode shall be made from a silver wire, 2 mm in diameter or larger, mounted in an insulated support.

4.2.3 Meter¹⁾, for instance an electronic voltmeter, operating on an input of less than 9×10^{-12} A and having a sensitivity of ± 2 mV over a range of at least ± 1 V. The meter shall be electrostatically shielded, and the shield shall be connected to ground.

4.2.4 Titration stand, preferably built as an integral part of the meter housing and provided with supports for the electrodes and electrical stirrer, all connected to ground. No permanent change in meter reading shall be noticeable upon connecting or disconnecting the stirring motor.

4.2.5 Emery cloth or paper, having an average particle size of 18 μm .

4.3 PREPARATION OF APPARATUS

4.3.1 Glass electrode

Before and after each titration, wipe the electrode with a soft, clean tissue and rinse with water. Clean the electrode at frequent intervals (at least once every week during continual use) by stirring in cold chromic acid cleaning solution for a few seconds. When not in use, keep the lower half of the electrode immersed in water.

4.3.2 Silver/silver sulphide electrode

Each day, prior to use, prepare a fresh silver sulphide coating on the electrode in the following manner: Burnish with an emery cloth or paper (4.2.5) until a clean, polished silver surface shows. Place the electrode in the operating position and immerse it in 100 ml of titration solvent containing 8 ml of sodium sulphide solution (4.1.2). Add slowly from a burette, with stirring, 10 ml of silver nitrate solution (4.1.5) over a period of 10 to 15 min. Remove the electrode from the solution, wash with water, and wipe with a soft, clean tissue. Between titrations, store the electrode for at least 5 min in 100 ml of titration solvent containing 0,5 ml of silver nitrate solution (4.1.5).

4.4 PROCEDURE

4.4.1 If hydrogen sulphide (H_2S) is known to be absent, proceed as directed in 4.4.2 to 4.4.5. If the sample is of

unknown composition, remove the hydrogen sulphide as described in 3.4.1.

4.4.2 Measure with a pipette (see note 1 to 3.4.2), or weigh, 20 to 50 ml of the original or treated sample into a 300 ml titration beaker containing 100 ml of titration solvent. Immediately place the beaker on the titration stand and adjust its position so that the electrodes are about half immersed. Fill the burette with alcoholic silver nitrate solution (4.1.6) and place the burette in position in the titration assembly so that the tip extends approximately 25 mm below the surface of the liquid in the beaker. Adjust the speed of the stirrer to give vigorous stirring without spattering.

4.4.3 Record the initial burette and cell potential readings. Add suitable small portions of silver nitrate solution (4.1.6) and, after waiting until a constant potential has been established, record the burette and meter readings. Consider the potential constant if it changes less than 6 mV per min.

4.4.4 When the potential change is small for each increment of silver nitrate solution, add volumes as large as 0,5 ml. When the change of potential becomes greater than 6 mV per 0,1 ml, use 0,05 ml increments of silver nitrate solution (4.1.6). Near the end point of the titration, 5 or 10 min may elapse before a constant potential is obtained. Although it is important to wait for equilibrium conditions, it is also important that the duration of the titration be as short as possible in order to avoid oxidation of the sulphur compounds by atmospheric oxygen. Once started, a titration must never be interrupted and resumed later.

NOTE — If potential readings obtained with freshly prepared electrodes are erratic, it is possible that the electrodes are not properly conditioned. This difficulty usually disappears in succeeding titrations.

4.4.5 Continue the titration until the meter reading has passed + 350 mV (see note) and the change of cell potential per 0,1 ml of silver nitrate solution (4.1.6) has become relatively constant. Remove the titrated solution, rinse the electrodes well, first with alcohol and then with water, and wipe with a dry tissue. Burnish the silver electrode lightly with an emery cloth or paper (4.2.5). Between successive determinations on the same day, immerse the electrodes in 100 ml of titration solvent containing approximately 0,5 ml of silver nitrate solution (4.1.5).

NOTE — With certain instruments, the algebraic sign of the potentials may appear reversed.

1) Any apparatus that will give equal or better precision will be acceptable.

4.5 INTERPRETATION OF RESULTS

4.5.1 Treatment of data

Plot the cumulative volumes of silver nitrate solution (4.1.6) added against the corresponding cell potentials. Select the end point at the most positive value of the steepest portion of each "break" in the titration curve as shown in figure 3 (see note to 4.4.5).

4.5.2 Mercaptans only

If mercaptans alone are present in the sample, the titration produces a curve of the first type shown in figure 3, having a plateau in the vicinity of - 300 to - 350 mV and an end point at about + 300 mV.

4.5.3 Mercaptans and elemental sulphur

4.5.3.1 When elemental sulphur and mercaptans are both present in the sample, a chemical interaction occurs which, in the titration solvent used, precipitates silver sulphide (Ag₂S) during the titration.

4.5.3.2 When mercaptans are present in excess, the end of the silver sulphide precipitation occurs at about - 500 to - 350 mV, and is followed by the precipitation of the silver mercaptide to the + 300 mV end point. This situation is shown in the middle curve of figure 3. Since all of the silver sulphide originates from an equivalent amount of

mercaptan, the total titration of the mercaptide end point must be used to calculate the amount of mercaptan sulphur.

4.5.3.3 When elemental sulphur is present in excess, the end of the silver sulphide precipitation is taken in the same region (+ 300 mV) as in the case of silver mercaptide, and is calculated as mercaptan sulphur.

4.6 CALCULATION

The mercaptan sulphur content, as a percentage by mass, of the sample is given by the formula

$$3,206 \frac{VT}{m}$$

where

V is the volume, in millilitres, of silver nitrate solution required;

T is the normality of the silver nitrate solution;

m is the mass, in grams, of the test portion.

4.7 PRECISION

The precision of this method is the same as that of the amperometric method (see clause 3).

4.8 TEST REPORT

Report the mercaptan sulphur content as calculated in 3.5 or 4.6 and make reference to this International Standard.

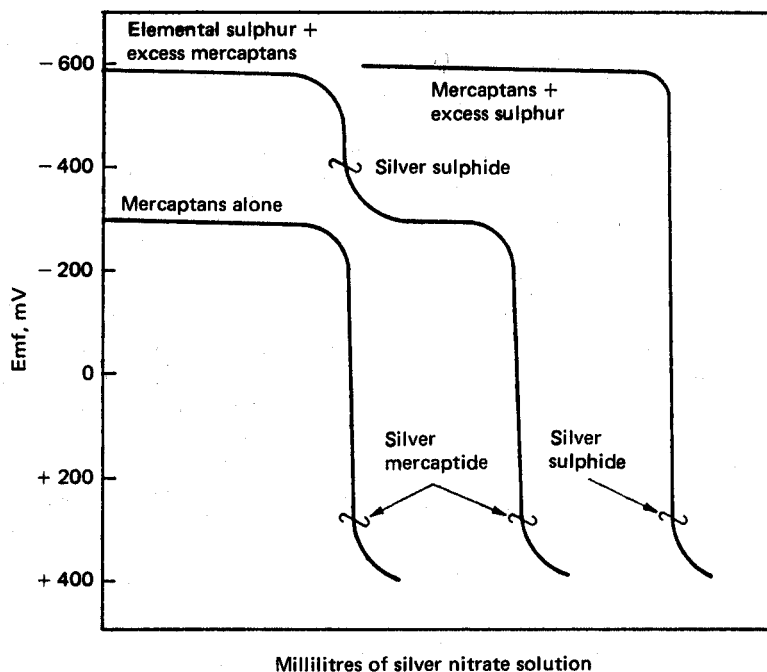


FIGURE 3 – Illustrative potentiometric titration curves