

W45C 1978

Analysis Method
No. 7

SB Casting
Powder Nb. 1

27.6.1952

J. Williams

METHODS OF ANALYSIS.
(E.R.D.E., WALTHAM ABBEY.)

METHOD NO. 7.
S.B. CASTING POWDER NO.1.
27.6.1952.
Amended 20.1.1953.

A. GENERAL REMARKS.

The nominal composition of S.B. Casting powder No.1. is

Nitrocellulose (wood, 12.2%N.)	88.0%
Lead stearate	5.0%
Diethylphthalate	5.0%
2-Nitrodiphenylamine	2.0%
Graphite glaze	0.05%

The casting powder is supplied as chopped cord 0.03 inch diameter and 0.03 inch long.

Diethylphthalate and 2-nitrodiphenylamine are separated from the nitrocellulose, lead stearate and graphite by extraction with boiling ether. To expedite the extraction, the propellant is ground to pass a 36 mesh British Standard Test sieve, as extraction of the unground propellant may take several days for completion. The ether dissolves some stearic (and/or palmitic) acid derived from the lead stearate, but the amount of lead dissolving is negligibly small. The dissolved acid does not interfere with the subsequent determinations of diethylphthalate or 2-nitrodiphenylamine, but it is necessary to determine the amount dissolved if the weight of ether-soluble material is used to derive a value for the nitro-cellulose content.

The nitrocellulose content is derived from the weight of ether-insoluble matter. To the ether-insoluble matter is added the stearic (palmitic) acid and the nitrocellulose dissolved by the ether; from the sum is deducted the graphite and lead stearate to give the nitrocellulose.

The "lead stearate" incorporated in S.B. Casting Powder No.1. is prepared from a mixture of stearic and palmitic acids. It is determined by conversion to sulphate, organic matter being simultaneously removed by oxidation. The factor connecting lead sulphate and lead stearate must be determined on the lead stearate as supplied for incorporation in the casting powder.

Diethylphthalate is determined by saponification, after it has been extracted from the powder with ether. The ether-soluble matter also contains 2-nitrodiphenylamine and a little soluble nitrocellulose. The intense colour of the 2-nitrodiphenylamine interferes with the end-point of the titrations if indicators are used, although it does not interfere with the end-point determined by glass electrode and pH meter. The amount of soluble nitro-cellulose is sufficient to introduce a serious error in the saponification value, as it is itself hydrolysed, and it must therefore be removed before saponifying the diethylphthalate. In the method described both 2-nitrodiphenylamine and soluble nitro-cellulose are removed simultaneously by treatment with titanous chloride or sulphate.

2-Nitrodiphenylamine is most conveniently determined by absorption spectrometry, for which purpose the casting powder may be dissolved direct in acetone, or alternatively a solution of the ether-soluble materials in a suitable solvent may be employed.

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If absorption spectrometry cannot be used, the amine can be determined by reduction with titanous sulphate after removing the dioctylphthalate whose presence tends to give low results by preventing contact between the amine and the reducing agent.

The graphite glaze is removed from the surface of the granules of unground powder by quick treatment with concentrated sulphuric acid. Organic matter and lead sulphate mixed with the graphite are removed by suitable treatment, and the graphite finally determined by burning off at 800°C.

B. TESTS AND DETERMINATIONS.

1. Volatile matter in sample as received.
2. Volatile matter in sample ground for analysis.
3. Nitrocellulose.
4. Lead stearate.
5. Dioctylphthalate.
6. 2-Nitrodiphenylamine.
7. Graphite glaze.

C. SPECIAL REAGENTS.

C.1. For Lead Stearate Estimation

1.1. 60% sulphuric acid (v.v.)

Mix equal volumes of concentrated sulphuric acid and 2N sulphuric acid.

1.2. "Lead Acid"

Mix 300 ml. concentrated sulphuric acid and 1800 ml. water. Dissolve 1g. pure lead acetate in 300 ml. water and add this to the hot solution, stirring meanwhile. Stand 24 hours and filter through a thick asbestos pad.

1.3. Ammonium acetate, saturated solution in water

C.2. For Dioctylphthalate

2.1. 0.2 N Titanous solution in 2N hydrochloric acid

Dilute 100 ml. concentrated hydrochloric acid to 800 ml. with water. To this solution add 200 ml. commercial 15% titanous chloride or sulphate. Store in a well-stoppered bottle, preferably containing a layer of zinc amalgam about half an inch deep if the solution is to be kept more than a few days. Shake thoroughly before use.

C.3. For 2-Nitrodiphenylamine

3.1. 0.1 N Titanous sulphate in 3N (approx.) sulphuric acid

Carefully add approximately 150 ml. concentrated sulphuric acid from a measuring cylinder to approximately 600 ml. distilled water in a 2 litre bolt-head flask. Add 250 - 260 ml. commercial titanous sulphate solution (containing 15 - 20% titanous sulphate), boil 2-3 min. till the vapour is free from hydrogen sulphide. Dilute to about 2 litres with recently boiled and cooled distilled water. Store under an inert atmosphere in a suitable container and dispenser.

3.2. 0.1 N Ferric sulphate

Dissolve a known weight (approximately 11.2g.) of iron

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of known purity in a mixture of 70 ml. concentrated sulphuric acid (Analar) and 400 ml. water. H.S. brand electrolytic iron rod as supplied by Messrs Johnson Matthey for spectrographic work is suitable. When solution is complete, add concentrated potassium permanganate solution slowly from a burette until the solution becomes tinged pink-brown by a small excess of permanganate; the permanganate used towards the end of the addition should be weak (e.g. 0.02N). Boil the solution for a few minutes to destroy excess permanganate and remove dissolved oxygen, cool, and dilute with boiled-out distilled water to 2 litres in a standard flask. Label with the calculated strength of the solution of ferric sulphate.

3.3. Ammonium thiocyanate indicator, 10% aqueous

Dissolve 10 g. ammonium thiocyanate in sufficient boiled-out cooled water to give 100 ml. solution.

3.4. Sodium citrate solution, 20% aqueous

Dissolve 20 g. sodium citrate (Analar) in about 95 ml. warm, boiled-out, distilled water. Allow to cool in the bottle in which it is to be stored, passing a slow stream of oxygen-free carbon dioxide through the solution during the cooling. Store in a well stoppered bottle with only a small air space over the solution.

D. PROCEDURE.

D.1. Preparation of Sample

Prepare a stock of powder ground to pass a 36 mesh British Standard Test Sieve. An all-through grinding is required; this is best obtained by sieving the ground material each time it passes through the mill, the portion retained on the 36 mesh sieve being reground. The whole of the casting powder taken for grinding must pass the sieve; the combined material after passing the sieve must be blended and stored in a rubber-stoppered bottle.

D.2. Volatile Matter in Sample as Received

Determine the total volatile matter in the sample as received by the cone and dish with gelatiniser procedure described in E.R.D.E. Method No. 3. (Total Volatile Matter in Colloidal Propellants).

D.3. Volatile Matter in Sample ground for Analysis

Determine as for volatile matter in sample as received.

D.4. Nitrocellulose

Place a Soxhlet extraction thimble (paper or alundum) in a suitable weighing bottle, dry in an oven at 100 - 105°C. with weighing bottle open for an hour, cool in a desiccator for a standard time (20 mins.) with the lid on and weigh. Transfer 5 g. of ground casting powder, weighed roughly in a scoop, to the thimble, return the latter to its weighing bottle and re-weigh to obtain by difference the accurate weight of powder taken. Extract with ether in a Soxhlet apparatus for at least six hours, using a 250 ml. conical flask as receiver. Keep the ether solution for the determination of dissolved stearic acid as described below.

Remove the bulk of the ether from the ether-insoluble matter by placing the thimble in a beaker on top of an oven (oven temperature 100 - 105°C.). Empty the contents of the thimble into the weighing bottle, add 20 ml. distilled water, and evaporate

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to dryness by suspending the bottle in a boiling water bath. Replace the thimble in the bottle, finally dry to constant weight at 105°C. to obtain the weight of ether-insoluble matter.

Remove the ether from the solution of ether-soluble material by distillation, blowing off the last traces with a stream of air. Dissolve the residue in 50 ml. 98% alcohol, and titrate with standard 0.1N. sodium hydroxide using phenolphthalein indicator. (Keep this solution for the determination of dioctylphthalate as in D.6. below). Run a blank determination on 50 ml. 98% alcohol. From the difference (v ml.) between the titrations, calculate the amount of stearic acid dissolved by the ether, using the expression:-

% Stearic acid dissolved by ether =

$$\frac{v \times f \times 0.0284 \times 100}{w}$$

where v is the difference between titrations,
f is factor of the 0.1 N sodium hydroxide,
w is weight of ground powder.

(The V.M. can be ignored, as its effect is negligibly small).

Calculation of Nitrocellulose Content

1. Calculate the amount of ether-insoluble material as a percentage of the powder free from V.M. Call the result A%.
2. Add to A the percentage of stearic acid dissolved by the ether. Call the result B%.
3. Add to B the figure 0.35 to correct for the nitrocellulose dissolved by the ether. (The solubility of wood N.C., 12.2% N. in ether is taken as 0.4%). Call the result C%.
4. Subtract from C the percentage of lead stearate in the powder free from V.M., determined as in D.5. below. Call the result D%.
5. Subtract from D the percentage of graphite glaze determined as in D.8. below. (The quantity of graphite glaze is usually so small that it can be ignored). Call the result E%.
6. The quantity E% (or D% if no correction for graphite glaze is applied) is the percentage of nitrocellulose in the casting powder, free from V.M.

D.5. Lead Stearate

Place approximately 5 g. unground casting powder, accurately weighed, in a 200 ml. Kjeldahl flask. Add 30 ml. concentrated nitric acid (s.g. 1.42) followed by 20 ml. concentrated sulphuric acid (s.g. 1.84). Place a small funnel in the mouth of the flask to act as a splash-trap. Clamp the flask in a sloping position in a fume cupboard. Warm gently with a small bunsen flame till reaction commences, then remove flame. When effervescence slackens resume heating over a small flame to maintain the action. After about half an hour the nitric acid has been exhausted; the reaction decreases and the solution becomes black. Increase the heat and add concentrated nitric acid a few drops at a time until the solution no longer darkens on continued heating. The colour is yellow-orange. Heat the solution to fuming. Allow to cool to room temperature, then pour into 50 ml. water in a beaker and wash out the flask thoroughly into the beaker with a further 100 ml. water. Stand at least 5 hours to ensure complete separation of the lead sulphate. Collect the lead sulphate on a

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Gooch crucible or a sintered silica crucible (No.4). Wash thrice with lead acid then thrice with alcohol. Dry at 130°C. and then transfer to muffle furnace at 500°C. for 15 minutes, cool and weigh. Dissolve out the lead sulphate with a saturated solution of ammonium acetate, wash thoroughly with water and alcohol, dry at 130°C. and reheat at 500°C. in muffle furnace for 15 minutes. The loss in weight during the ammonium acetate extraction gives weight of lead sulphate, which is converted to lead stearate by the appropriate factor.

Graphite glaze does not interfere in the above procedure. It is partially destroyed during the oxidation, but very little is lost during the heating at 500°C.

Calculate the percentage of lead stearate in the powder free from V.M. and graphite, using the expression:

$$\% \text{ lead stearate} = \frac{w_1 \times f \times 100}{w_2} \times \frac{100}{100 - a}$$

where w_1 is weight of lead sulphate found,
 f is factor connecting lead sulphate and stearate,
 w_2 is weight of powder taken,
 a is sum of percentages of T.V.M. and graphite in powder taken.

Determination of Factor

The composition of the lead stearate used in manufacture does not correspond to a simple salt. The factor for converting lead sulphate to lead stearate must therefore be determined on a sample of the lead stearate by the method described above for the determination of lead in the propellant. Take approximately 0.2 - 0.3 g. lead stearate for the determination. Then if a grams lead stearate gives b grams lead sulphate, $f = \frac{a}{b}$

D.6. Dioctylphthalate

Determine the dioctylphthalate in the neutralised alcoholic solution which resulted from the determination of soluble stearic acid (D.4.). Warm the solution to about 50°C., add 25 ml. 0.2 N titanous solution, stopper the flask and shake thoroughly till the colour of 2 - N.D.P.A. has disappeared (several minutes). Cool to room temperature, transfer to a 250 ml. separating funnel and extract thoroughly with petroleum ether b.p. 40 - 60°C, the following procedure being suitable.

After pouring the contents of the flask into the (first) 250 ml. separating funnel, wash the flask with 30 ml. petroleum ether, and pour the petroleum ether into the first funnel. Shake well, releasing pressure at intervals. Allow the layers to separate. The petroleum ether layer should be almost colourless as a very small quantity of 2 - N.D.P.A. obscures the end point of subsequent titrations. Run the lower aqueous layer into a second separating funnel, and the petroleum ether layer into a third. Wash the flask with 30 ml. petroleum ether, transfer the petroleum ether to the second funnel and extract as before. After separation run the lower aqueous layer into the first funnel and the petroleum ether into the third. Wash the flask again with 30 ml. petroleum ether, transfer the petroleum ether to the first funnel, and extract as before. After separation, reject the lower aqueous layer, and run the petroleum ether into the third funnel. Wash the petroleum ether in the third funnel with two lots of water, 30 ml. each time, rejecting the water washings. Transfer the

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petroleum ether to a 250 ml. flask, and remove the petroleum ether by distillation completing the removal with a gentle stream of air.

Dissolve the residue in the flask in 25 ml. 98% alcohol. Add 1 ml. phenolphthalein indicator, then neutralise with 0.1 N sodium hydroxide. Similarly neutralise 25 ml. alcohol in a second flask to act as a blank. Add from a pipette to each flask 25 ml. 0.2N alcoholic potash (containing 10% water to avoid precipitation of potassium phthalate during hydrolysis, with consequent bumping). Hydrolyse under reflux for one hour. Wash down each condenser with 20 ml. of boiled and cooled water into its flask. Titrate the contents of the flasks with 0.1 N hydrochloric acid.

Calculation

A rather wide range of ester value (98 - 103 %) is permitted in the specification for dioctylphthalate. For the most accurate assessment of the quantity of dioctylphthalate in the casting powder, the ester value of the phthalate incorporated in the powder must be known. It is generally sufficiently accurate to assume the ester value to be 100%, and use the theoretical factor, 0.1953 g. dioctylphthalate corresponding to 1 ml. of N hydrochloric acid. Subtract the acid titre of the determination from the acid titre of the blank to get the acid equivalent to the alkali consumed in hydrolysis. Then use the above factor to calculate the percentage of dioctylphthalate in the casting powder free from volatile matter and graphite.

% Dioctylphthalate in casting powder free from V.M. and graphite is:-

$$v \times f \times 0.01953 \times \frac{100}{w} \times \frac{100}{(100-a)} \times F$$

where v is difference between volumes of determination and blank.

f is factor of 0.1 N hydrochloric acid,

F is apparent purity of dioctylphthalate as indicated by its ester value,

w is weight of ground casting powder extracted,

a is sum of percentages of T.V.M. and graphite in the ground powder.

D.7. 2-Nitrodiphenylamine

1. Spectro-photometric Determination

Weigh accurately 0.3 to 0.35 g. casting powder. Place in a dry 100 ml. standard flask. Add about 50 ml. acetone, stopper the flask and shake on the mechanical shaker till all the powder has dissolved (about 45 mins.). Make up to the mark with acetone. Compare the optical density of this solution with a standard solution of 2-nitrodiphenylamine in acetone, containing about 5 mg. per 100 ml., by the relative method described in Methods of Analysis, E.R.D.E., Waltham Abbey, No. 6. (2-Nitrodiphenylamine; Spectrophotometric Determination), and thus obtain the concentration of 2-nitrodiphenylamine in the acetone. Hence calculate the total quantity in the acetone, and finally the percentage of 2-nitrodiphenylamine in the casting powder free from volatile matter and graphite.

The above method is very quick but tends to give slightly high results owing to "background" in optical density due to dissolved materials. Greater accuracy may be obtained at

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the expense of time by using the ether-soluble material extracted from the ground powder. Extract a suitable quantity, which may range from 0.3 to 5 g., with ether in a Soxhlet extractor. Remove ether by the usual procedure, dissolve the residue in ethyl alcohol, bulk to known volume and dilute to obtain a concentration suitable for measurement of optical density. From the optical density, measured either by the absolute or relative method, calculate the concentration of 2-nitrodiphenylamine in solution, and hence the percentage of 2-nitrodiphenylamine in the powder free from volatile matter and graphite.

2. Chemical Determination

Extract about 5 g. of ground casting powder, accurately weighed by the technique described in D.4. with ether in a Soxhlet extractor for at least six hours, using a 300 ml. carbon dioxide flask as receiver. Distil the ether from the soluble extract, removing the last traces in a gentle stream of air. Add 25 ml. 0.2 N alcoholic potash (containing 10% water) and reflux for one hour. Reflux a blank of 25 ml. 0.2 N alcoholic potash (containing 10% water) at the same time as the determination. At the end of reflux, wash down each condenser with 10 ml. water into its flask. Add phenolphthalein indicator, and neutralise with 0.1 N hydrochloric acid.

Add 50 ml. of 20% sodium citrate solution (from measuring cylinder) to each flask. Close each flask with a bung carrying a gas inlet tube, and pierced by a fairly large hole through which the jet of a burette may be loosely inserted. Bubble carbon dioxide through the alcoholic solution for 5 mins. From a burette add 5 ml. of 0.1 N titanous sulphate to the blank, and a known volume (A ml.) to the determination, sufficient to give an excess of about 5 ml. The quantity required may be calculated or found by trial; it is approximately 30 ml. Continue to pass carbon dioxide for a further three minutes, then remove the bung and add 17 ml. concentrated hydrochloric acid (from a measuring cylinder). Swirl to mix thoroughly, then add 20 ml. 10% ammonium thiocyanate (measuring cylinder). It is essential to mix the acid thoroughly before adding the thiocyanate. Titrate with 0.1 N ferric sulphate to the red ferric thiocyanate end point, persisting for at least 30 secs. (B ml. ferric sulphate for the determination, and C ml. ferric sulphate for the blank).

Titrate several 20 ml. aliquots of 0.1 N titanous sulphate with 0.1 N ferric sulphate. Use the average of these titrations to standardise the titanous sulphate solution; let the average be D ml. ferric sulphate. Also calculate the volume of the ferric sulphate which would be equivalent to 5 ml. titanous sulphate (i.e. $D/4$) = E ml. ferric sulphate.

Calculation

The A ml. titanous sulphate added in the test determination is consumed by the 2-nitrodiphenylamine and by the impurities in the reagents, while some remains as an excess. The excess is titrated directly, being equivalent to B ml. ferric sulphate.

The amount consumed by the reagents is found from the blank. As 5 ml. titanous sulphate is equivalent to E ml. ferric sulphate, the amount consumed by the reagents is (E - C) ml. ferric sulphate.

Then the excess titanous sulphate plus the amount consumed by reagents are together equivalent to (B + E - C) ml. ferric sulphate.

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Then as the A ml. titanous sulphate used in the determination is equivalent to $(A \times \frac{D}{20})$ ml. ferric sulphate, the amount of titanous sulphate used by the 2-nitrodiphenylamine is equivalent to

$$(A \times \frac{D}{20}) - (B + E - C) \text{ ml. ferric sulphate.}$$

= v ml. ferric sulphate.

Calculate the percentage of 2-nitrodiphenylamine in the powder free from V.M. and graphite using the expression:

$$\% \text{ 2-N.D.P.A.} = v \times f \times 0.00357 \times \frac{100}{w} \times \frac{100}{100-a}$$

where v = volume of ferric sulphate calculated above,
 f = factor of 0.1 N ferric sulphate,
 w = weight of powder extracted,
 a = sum of percentages of T.V.M. and graphite in the ground powder.

Note on Quantity of Titanous Sulphate Solution

Not more than 35 ml. of titanous sulphate in 3N sulphuric acid may be added to 50 ml. 20% sodium citrate solution; if more is used the pH of the final solution will be too low. If the titanous sulphate is prepared in sulphuric acid stronger than 3N, the maximum volume which may be used is correspondingly smaller.

D.8. Graphite Glaze

Transfer 5 ± 0.01 g. of unground casting powder, weighed in an aluminium scoop, to a 300 ml. beaker. Cover with 10 ml. concentrated sulphuric acid, stir for 10 secs. then immediately dilute with 200 ml. water, stirring vigorously during the addition. Allow the granules of propellant to settle to the bottom of the beaker, then decant the aqueous suspension of graphite and other suspended matter into a beaker. Wash the granules with two 25 ml. portions of water to remove all graphite. Filter the suspension through a silica Gooch crucible (porosity 4), previously ignited at 800°C. If the crucible becomes clogged during the filtration it may be cleared by the addition of a little hot water, or by flushing through with acetone. Wash the crucible thrice with acetone, then with saturated ammonium acetate solution. Finally wash with water and finish with acetone. Dry at 110°C for 1 hour, cool and weigh. Ignite at 800°C. for 30 mins., cool and reweigh. The loss in weight during ignition gives the amount of graphite glaze. Calculate the percentage of graphite glaze in the sample as received, using the expression:

$$\% \text{ graphite} = \frac{w_1}{w_2} \times 100$$

where w₁ = weight of graphite determined above,
 w₂ = weight of casting powder used.