Sample No.	I Appearance of Water Solution	II PER CENT FAT Flask Method	III PER CENT FAT New Method	IV Per Cent Yield (a)	V Acid Value of Fatty Acids	VI PER CENT NH ₃ Added	VII New Method	VIII PER CENT BOUND SO ₃ Gravimetric Method	IX New Method
1(b)	Opalescent(e)	73.5	73.7	95.3	188	1.81	1.81	5.78	5.63
2	Opalescent(e)	77.0	77.1	96.0	188	None	...	...	...
3	White Emulsion	73.8	74.2	95.7	188	None	...	4.12	4.09
4	White Emulsion	78.5	78.3	96.3	188	None	...	...	...
5(c)	Clear Soluble	36.6	36.0	95.4	188	0.740	0.733	2.04	1.87
6(c)	Clear Soluble	32.6	32.1	95.5	188	0.375	0.385	1.75	1.64
7(d)	Opalescent	82.5	83.0	...	188	None	...	...	...
8	Opalescent(e)	60.1	59.0	...	Assumed 190	...	0.364	...	...
9	Opalescent(e)	68.5	69.0	...	Assumed 190	...	None	...	...
10	Clear Soluble	40.4	40.1	...	Assumed 190	...	None	...	...

(a) Average yield 95.7%; theory 96.0%. (b) Neutralized entirely with ammonia. (c) Neutralized partly with ammonia.

(d) Sulfated castor oil soap. (e) Changes to white emulsion on standing or on warming.

The net change in acidity, which is given by the titration, is equal to the difference between the total alkalinity due to the soap and the acidity due to the NaHSO₄. The total alkalinity of the original sample is obtained as above. Hence, the acidity corresponding to NaHSO₄, or combined SO₃, can be calculated. It is to be noted that 80 parts SO₃ is equivalent, in this case, to 56.1 parts of KOH. Cols. VIII and IX give the results obtained by the gravimetric method and our present method, respectively.

PROCEDURE

Below is given in detail the analysis of a Turkey-red oil which was partially neutralized with ammonia. The solutions required are: standardized $N/2$ H₂SO₄, $N/2$ NaOH, and approximately $N/2$ alcoholic NaOH. All titrations were made in presence of methyl orange, unless otherwise indicated.

TOTAL ALKALINITY—Ten grams were weighed into a 250 cc. Erlenmeyer flask, balanced on a scale sensitive to 5 mg. (all weighings were made in this manner), 150 cc. water added, and titrated with $N/2$ H₂SO₄. The titer of the acid was 27.02 mg. KOH, and the titration required 17.2 cc.

$$\text{Total alkalinity} = \frac{17.2 \times 27.02}{10} = 46.5 \text{ mg. KOH per g.}$$

ALKALINITY AFTER NH₃ WAS VOLATILIZED—Eight grams were dissolved in 100 cc. water in a 500 cc. beaker, 25 cc. $N/2$ NaOH added, and gently boiled until litmus paper no longer indicated ammonia (about one-half hour). Water was added and the alkali titrated with $N/2$ H₂SO₄. The titer of the caustic was 27.30 mg. KOH, the acid 27.02, and it took 31.85 cc. of the latter for the titration.

Alkalinity without ammonia

$$= \frac{31.85 \times 27.02 - 25 \times 27.30}{8} = 22.3 \text{ mg. KOH}$$

Should the sample contain a high percentage of fat (shown by the high viscosity and also by the fact that such samples give with warm water white emulsions) double the amount of caustic soda should be used.

From the above data, the ammonia was calculated as follows:

$$\text{Ammonia} = 46.5 - 22.3 = 24.2 \text{ mg. KOH, or, } 0.733 \text{ per cent NH}_3.$$

SAPONIFICATION VALUE—Eight grams were weighed into a 250 cc. Erlenmeyer flask provided with a long glass tube to serve as a reflux condenser, and 25 cc. $N/2$ alcoholic NaOH added. The flask was heated on a steam bath for 45 minutes, neutral alcohol added, and excess NaOH titrated with $N/2$ acid in presence of phenolphthalein. The blank took 23.4 cc. of acid, the titration required 9.95 cc., and the titer was 27.02.

$$\text{Saponification value} = \frac{(23.4 - 9.95) 27.02}{8} = 45.4 \text{ mg. KOH}$$

The alcoholic caustic should be filtered to remove carbonate. The titration should be carried out immediately after saponification, as otherwise the absorption of CO₂ from the air makes the end-point

indistinct. Double the amount of caustic should be used for concentrated samples.

The acid value of the castor oil fatty acid being known (188) the fat was calculated as follows:

$$\text{Fat} = \frac{22.3 + 45.4}{188} = 36.0 \text{ per cent}$$

COMBINED SULFURIC ANHYDRIDE—Eight grams were gently boiled for one hour with 25 cc. of standardized H₂SO₄ solution in a 300 cc. Erlenmeyer flask, provided with a condenser as for saponification. The flask was frequently shaken. Before disconnecting, the condenser was washed out with water by a spray from a wash bottle. The sample was then titrated with caustic soda. The end-point was best observed by adding excess alkali and finishing the titration with acid. It took 21.15 cc. of the alkali to neutralize the excess acid; the titer of the alkali was 24.48 and of the acid 31.4 (in the calculation, it should be kept in mind that the acid is partly neutralized by the alkali in the oil, which, in this case, is equivalent to 46.5 mg. KOH).

$$\text{Combined SO}_3 = \left(\frac{21.15 \times 24.48 - 25 \times 31.4}{8} + 46.5 \right) \frac{80}{56.1} = 1.87 \text{ per cent}$$

CONCLUSIONS

I—Turkey-red oils and similar products are completely or nearly completely saponified by $N/2$ alcoholic NaOH.

II—Alkali bound as soap can be determined by titrating its solution with acid in presence of methyl orange.

III—It is feasible to calculate the combined SO₃ from the increase in acidity due to the splitting of the sulfo group.

IV—Based on these fundamentals a rapid method has been developed whereby sulfated oils can be analyzed for fat, ammonia and caustic soda bound as soap, and for sulfuric anhydride in the form of sulfo-ricinoleic acid.

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THE DETERMINATION OF TANTALUM IN ALLOY STEELS

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The number of methods so far published for the determination of tantalum in steels is small. Most of these deal with the determination of the element in a carbon steel and do not indicate methods available for use with steels of a more complex character. The methods outlined below may be used for the determination of tantalum in steels containing nickel, cobalt, aluminum, chromium, vanadium and tungsten in addition to other elements usually present in steel. Titanium interferes.

PROCEDURE IN THE ABSENCE OF TUNGSTEN

The weight of the sample should be 1 g. for 2 to 5 per cent tantalum steels, 2 g. for those containing 0.5 to 2 per cent and up to 10 g. for lower percentages. The sample is best dissolved in 1:1 hydrochloric acid with heat, and evaporated to dryness. The residue is treated with hot dilute HCl, boiled for a few minutes, and the solution filtered. Both the filtrate and the residue on the filter paper are to be saved. The filtrate is next evaporated to small volume, during which process the iron is oxidized by the addition of a small amount of nitric acid to the boiling solution. When the bulk has been reduced to a point where the solution has a syrupy consistency, 50 cc. of concentrated hydrochloric acid are added and the evaporation repeated. On cooling, the iron may be extracted from the solution with ether. The aqueous layer is then boiled to remove dissolved ether and treated with a slight excess of ammonia to precipitate the tantalum. If more than traces of chromium and vanadium are present, after extraction with ether, the solution should be evaporated with 15 cc. of sulfuric acid (sp. gr. 1.58) until fumes appear. It is then carefully diluted with hot water to a volume of 300 cc., and 20 cc. of a solution of silver nitrate (1 g. in 1 liter) and 3 g. of ammonium persulfate added, after which it is further boiled. This oxidizes the chromium and vanadium to chromate and vanadate, in which state they do not interfere with the determination. Ammonia in slight excess is then added as above and the solution boiled again. The precipitate in any case will contain all of the tantalum and aluminum which was in solution, together with variable, but generally small amounts of chromium, vanadium and manganese. The solution is filtered and the precipitate after washing is combined with the insoluble residue collected in the first filtration. The precipitates are ignited in a platinum crucible at a moderate temperature in order to avoid making the subsequent solution of aluminum and chromium difficult. Two to five grams of fused potassium acid sulfate were then added and the whole fused several minutes at a moderate temperature. The fused mass is then leached with hot 1:1 hydrochloric acid and filtered. SiO_2 and Ta_2O_5 are collected on the filter paper. This residue is now ready for ignition in a weighed platinum crucible. The residue in the crucible is treated with a few drops of concentrated H_2SO_4 and 2 to 5 cc. of hydrofluoric acid to remove silica. After evaporating the sulfuric acid and igniting, the residue is weighed as Ta_2O_5 . The factor is 0.82.

PROCEDURE WHEN TUNGSTEN IS PRESENT

The size of the sample is as described above. Solution is made in 1:1 hydrochloric acid which is oxidized while hot by the dropwise addition of nitric acid. The solution is then diluted with 4 volumes of water and boiled for several minutes. The tungstic oxide is then filtered out and washed thoroughly with water containing a little hydrochloric acid. The wash waters and filtrates are combined and evaporated until the solution has a syrupy consistency. Fifty cc. of concentrated HCl are then added and the evaporation re-

peated. At this point the ferric iron is extracted with ether and the aqueous layer saved. During the preceding evaporation there will usually be no separation of either SiO_2 or Ta_2O_5 , but if such a separation does occur the precipitate should be filtered out and treated like the tungstic oxide precipitate.

The precipitate of tungstic oxide should be washed into a beaker, and water and ammonia added to dissolve the tungstic compounds. The residue which may contain Ta and traces of Fe, W, Cr, etc., is collected on a filter paper and saved.

The aqueous layer left after the ether extraction is boiled to remove the ether, 15 cc. of sulfuric acid (sp. gr. 1.58) added, and the solution evaporated until fumes appear. The object is to remove chlorides. The solution is next carefully diluted to a volume of 300 cc. with hot water and 20 cc. of a solution of silver nitrate (1 g. in 1 l.) and 3 g. of ammonium persulfate added. Boiling one or two minutes oxidizes Cr, V and Mn. Ammonia then precipitates an impure hydrated tantalic oxide as described above, leaving most of the chromium and vanadium in solution. After boiling a few minutes, it is allowed to settle, and filtered. This precipitate is combined with the insoluble residue left after dissolving the tungstic oxide in ammonia. The procedure from this point is exactly as described under the procedure in the absence of tungsten except that the residue of Ta_2O_5 and SiO_2 obtained by leaching the bisulfate fusion with hydrochloric acid may in this case contain a little tungstic oxide. Therefore, after washing it with acid and water, it should be covered with a dilute solution of ammonia and finally washed with water. Ignition followed by treatment with hydrofluoric and sulfuric acids gives Ta_2O_5 .

It is to be noted that the precipitate obtained in the manner described above contains Cb_2O_5 if this is present. At this writing, it is not generally of interest to know separately the percentages of Ta and Cb present in a sample of steel, but where such information is desirable separation must be made by the known methods by work on the residue described in this paper as Ta_2O_5 .

EXPERIMENTAL

A sample of ferro-tantalum was analyzed by the method given by Arnold and Ibbotson. A portion of this sample which contained 3.5 per cent of Al besides about 70 per cent of Ta, was covered with hydrofluoric acid in a platinum dish and nitric acid added drop by drop. When the alloy was completely dissolved the solution was evaporated to perhaps half of its former volume. At this point 20 cc. of sulfuric acid (sp. gr. 1.58) were added and the solution again evaporated slightly. This gave a solution which remained clear several days on diluting with water. By calculation based upon the weight of the ferro-alloy taken, the strength of the solution was found to be such that 25 cc. contained 0.0105 g. of tantalum. To test our method 50 and 100 cc. portions of this solution were added to 2-g. portions of plain carbon, nickel-chromium and high-speed steels, the latter containing 4 per cent of chromium, 2 per cent of vanadium,

and 14 per cent of tungsten. Acid to dissolve the steel was then added and the analyses made as described above. The analytical results which we obtained in testing our method are given in the table below:

DETERMINATION OF TANTALUM IN THE PRESENCE OF CERTAIN OF THE CONSTITUENTS OF ALLOY STEELS
50 and 100 cc. portions of ferro-tantalum solution added to 2 g. samples of steel

KIND OF STEEL	No.	PER CENT TANTALUM	
		Added	Found
Plain Carbon.....	1	1.05	1.06
	2	2.10	2.05
Chromium-Nickel Steel.....	1	1.05	1.03
	2	2.10	2.10
Chromium-Vanadium-Tungsten Steel.....	1	1.05	1.00
	2	1.05	1.09
	3	2.10	2.05
	4	2.10	2.27

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NOTES ON THE ANALYSIS OF ALLOYS OF NICKEL AND ZIRCONIUM

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It recently became necessary in this laboratory to develop a convenient works-laboratory method for the analysis of an alloy of the following approximate composition:

Carbon.....	0.1 to 0.5 per cent	Aluminum....	0.5 to 10.0 per cent
Nickel.....	70.0 to 90.0 per cent	Zirconium....	2.0 to 18.0 per cent
Iron.....	2.0 to 6.0 per cent	Tungsten....	0.5 to 10.0 per cent
Silicon.....	2.0 to 8.0 per cent	Manganese....	0.1 to 0.3 per cent

An outline of the method used is given in this paper.

Dissolve one gram of the material, preferably of a fineness to pass a 40 mesh sieve, in 40 cc. of hydrochloric acid to which 20 cc. of nitric acid have been added; then evaporate the solution with 20 cc. of sulfuric acid (sp. gr. 1.58) until SO_3 fumes appear. On diluting with water the salts dissolve. Filtering separates nearly all of the tungsten as WO_3 and the silicon as SiO_2 , the zirconium appearing almost entirely in the filtrate.

Ignite the precipitate in a weighed platinum crucible. The first weight gives the weight of SiO_2 , WO_3 and impurities. Then treat the residue with hydrofluoric and sulfuric acids to remove SiO_2 , which is determined by the loss in weight: fuse the residue which now remains with sodium carbonate, leach with water and filter. The residue from leaching is generally very small and should be ignited in the original crucible and its weight subtracted from the weight of the crucible contents after the removal of SiO_2 ; this gives the weight of WO_3 . If extreme care is to be used in the determination of the tungsten, this residue should be fused with KHSO_4 , leached in dilute HCl and precipitated with ammonia. Under these circumstances iron, aluminum and zirconium are precipitated free from sodium compounds which may contaminate the first residue. Upon ignition a corrected residue is obtained to be subtracted from the weight of impure WO_3 . When such care is not necessary the residue may be fused with KHSO_4 and leached with the filtrate from the WO_3 precipitate.

By following the procedure as outlined above, the filtrate from the WO_3 contains in solution all of the iron, nickel, aluminum and zirconium. The solution should be made up to a convenient volume, such as 200 cc., and one-half taken for the iron determination.

To determine the iron, make the solution alkaline with ammonia and boil or heat near the boiling point for a short time; filter and wash the precipitate. Transfer the bulk of the precipitate to a beaker and wash the paper by running through it a small amount of dilute sulfuric acid. Add enough sulfuric acid to the beaker to dissolve the precipitate and an excess equivalent to 10 cc. of acid (sp. gr. 1.58). Then pass the solution through a Jones reductor and determine the iron by titration with KMnO_4 .

To the other half of the solution add ammonia in excess, and remove the nickel by electrolysis. The presence of this small amount of iron and aluminum does not seem to interfere, but in doubtful cases, the nickel may be dissolved in hydrochloric acid, evaporated with sulfuric acid, diluted and the iron and aluminum precipitated with ammonia; any iron and aluminum found in this way should be dissolved in a small amount of acid and added to the original electrolyte which now contains all of the iron, aluminum and zirconium. The ammoniacal solution of nickel is now free from the elements just named and is available for analysis by electrolysis or by the precipitation of its nickel content with dimethylglyoxime. In the event of using the latter procedure, one-tenth of the solution is sufficient for the purpose.

Boil the solution containing Al, Fe and Zr until nearly all of the ammonia has been driven off; then allow it to settle and filter, washing the precipitate with water. The precipitate contains Al, Fe and Zr. After transferring the precipitate to a beaker, dissolve in a minimum quantity of hydrochloric acid; then add solid KOH in excess to precipitate iron and zirconium, and leave aluminum in solution. Boil the mixture for one minute, allow to settle and filter, washing the precipitate with water. The filtrate contains the aluminum; make this solution acid with HCl and then barely ammoniacal; boil a few minutes, filter and wash. Then dissolve the precipitate in HCl and add 7 to 10 cc. of sulfuric acid (sp. gr. 1.58); evaporate the solution until fumes appear; cool, dilute and filter to remove SiO_2 . Again add ammonia in slight excess and after brief boiling remove the $\text{Al}(\text{OH})_3$ by filtration; ignite and weigh as Al_2O_3 .

Dissolve the precipitate of iron and zirconium hydroxides which was separated from the aluminum in HCl (1 : 1) and re-precipitate with ammonia while boiling. The ignited precipitate contains Fe_2O_3 and ZrO_2 . Convert the iron found by titration into Fe_2O_3 and subtract its weight from the weight of Fe_2O_3 and ZrO_2 . This gives the weight of ZrO_2 .

If manganese is to be determined, weigh 1.5 g. of the material instead of 1 g.; then determine manganese in one-third of the filtrate from the tungstic oxide. For this purpose add ammonia and ammonium persulfate to the solution before boiling. Wash and dissolve the precipitate in nitric acid with the addition of a little sodium sulfite or hydrogen peroxide to aid solution. The manganese is then ready for oxidation by sodium bismuthate and determination by the various known methods.

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