TABLE VI

Calculated Red Values—460 Millimicrons

Lab. No.	XS 275		Dif.	Variation from Av.		XS 276		Dif.	Variation from Av.	
	Sol. 1	Sol. 2		Sol. 1	Sol. 2	Sol. 1	Sol. 2		Sol. 1	Sol. 2
1	6.9	6.8	.1	.2	.1	3.7	3.7	0	0	0
2	6.3	6.8	.5	.4	.1	3.6	3.9	.3	.1	.2
3	7.9	6.7	(1.2)	(1.2)	(.0)	3.9	3.3	(.6)	(.2)	(.4)
4	5.6	6.7	(1.1)	(1.1)	(.1)	3.3	4.0	(.7)	(.4)	(.3)
5	6.7	6.8	.1	0	.1	3.7	3.7	0	0	0
6	6.7	6.8	.1	0	.1	3.7	3.7	0	0	0
7	6.9	6.6	.3	.2	.1	3.7	3.5	.2	0	.2
8	6.6	6.8	.2	.1	.1	3.7	3.8	.1	0	.1
9	7.0	6.7	3	.3	0	3.8	3.6	.2	.1	.1
10	6.6	6.8	.2	.1	.1	3.7	3.8	.1	0	.1
11	6.8	6.8	0	.1	.1	3.7	3.6	.1	0	.1
12	6.8	6.7	.1	.1	0	4.0	3.9	.1	.3	.2
13	6.7	6.7	0	0	0	3.8	3.8	0	.1	.1
14	7.0	6.8	.2	.3	.1	4.0	3.9	.1	.3	.2
15	6.7	6.8	.1	0	.1	3.8	3.8	0	.1	.1
16	6.4	6.8	.4	.3	.1	3.6	3.8	.2	.1	.1
17	7.0	6.8	.2	.3	.1	3.7	3.6	.1	0	.1
18	6.7	6.8	.1	.1	.1	3.6	3.7	.1	.1	0
	Avg. = 6.7					Avg. = 3,7				
	Avg. Deviation from Mean			0.156	0.081	Avg. Deviation from Mean			0.075	0.100
				= 0.195	0.101				= 0.094	0.125
		Lovibond Range		1.7			Lovibond Range		0.9	
		Photometric Range		0.4	0.1		Photometric Range		0.3	0.2

It seems quite possible that excellent agreement could be obtained between a large number of laboratories if only one or two corrected readings were used. Since the 460 correction factor for an oil of about 6.7 red is different from an oil of about 3.7, the obvious conclusion is that even at the 6.7 level a 25-mm. oil column is too long and that smaller columns or dilution will be necessary. In other words, it will be necessary to examine both darker and lighter oils to arrive at the proper column lengths and dilutions to use over a wider color range.

Conclusions

It may be concluded from the work of the committee during the past year that

1. eight of 18 instruments used in reporting requested data do not meet A.O.C.S. specifications. This conclusion is not necessarily a criticism of the instruments since only two of the instruments gave results materially out of line;
2. the use of standardizing solutions holds promise;
3. the possibility of using readings at only one or two appropriate wave-lengths suggests itself as a practical method of oil grading;
4. additional committee work is necessary not only in the direction so far taken but in other directions which may hold promise of giving precise instrumental color values.

G. W. AGEE
R. J. BUSWELL
W. T. COLEMAN
M. W. FORMO
SEYMORE GOLDWASSER
D. L. HENRY
DUNCAN MACMILLAN
E. J. WALLEN
C. L. MANNING
V. C. MEHLENBACHER
R. T. O'CONNOR
R. C. POPE
L. K. WHYTE
R. C. STILLMAN, chairman

[Received April 26, 1954]

Polarographic Determination of Titanium in Soap

JOSEPH HEJNA, Allen B. Wrisley Company, Chicago, Illinois

TITANIUM can be determined in soap polarographically after it is ashed, fused with potassium bisulfate, and dissolved in 1.0 N sulfuric acid solution saturated with sodium oxalate. The cathodic wave of the diffusion current is well defined and is in direct proportion to the concentration of the titanic ions. The polarographic method was compared with the colorimetric method. The percentage of titanium was substantiated by using the Ilkovic equation.

Mill-type of soaps contain titanium in the form of titanium dioxide, which is added as a whitener, also to make the bar opaque. The amount of titanium dioxide that is added to the soap will usually vary from 1 oz. to 8 oz. per 100 lbs. of soap, depending upon the desired color or opaqueness. In the course of soap analyses it becomes necessary at times to determine the amount of titanium dioxide, and it was with this object in mind that the polarographic method was investigated.

Preliminary Investigation

It was observed by Zeltzer (5) that the titanium gives well-defined waves in 0.1 N sulfuric, nitric, and hydrochloric acids. The wave of the diffusion current is due to the reduction of the titanic ions to the titanous state (5). Adams (1) found that 1.0 N sulfuric acid gives better reproducibility than 0.1 N sulfuric acid. Adams (1) used 8% urea as a maximum suppressor and saturated the solution with sodium oxalate to form the complex ion. The 1.0 N sulfuric acid was used as the electrolyte in the present investigation because potassium bisulfate was used to fuse the sample after it had been ashed. Sodium oxalate was used to form the titanium ion complex. Two other organic acids were investigated as to their complex formation, namely, tartaric and citric acids, but there was no evidence of any advantage over that of sodium oxalate. The use of urea was studied, and it was found that samples containing 8%, 6%, and 0% urea gave the same diffusion currents which caused us to decide not to use urea as a maximum suppressor. Inasmuch as the diffusion currents were the same with and without a suppressor, it was decided to use none. The effect of temperature change was studied, and it was found that there was approximately a 1% error per 1° change in temperature. This was studied between 20 and 30 degrees C.

Apparatus and Material

The polarograph was a Fisher Electropode. It is a manually operated instrument. The Electropode had no provision for thermostating, which was corrected for by placing the cell in a water bath that was thermostatically controlled at 25 ± .1°C. The galvanometer deflections are expressed in arbitrary units. The galvanometer was calibrated with a Weston microammeter so as to use the Ilkovic equation. The sample in the cell was deaerated with nitrogen from 10 to 20 minutes. The nitrogen was first passed through a 1.0 N sulfuric acid solution by means of a fine-porosity, fritted glass tube so as to saturate it before going to the cell. All the chemicals used were of reagent or C.P. grade.

Analytical Procedure

A standard solution of titanium sulfate was prepared from potassium titanium oxalate as described by Sandell (4). The standard solution was prepared to give a concentration of 1×10^{-2} moles per liter of titanium. From the standard solution the various dilutions were made, and the linear relation between the diffusion current and concentration was determined. With all other factors constant in Ilkovic equation (3) $i_d = KC$, where i_d is the average diffusion current in microamperes, C is the concentration of the titanium ions in millimoles per liter, and the constant K is equal to $605nD^{1/2}m^{2/3}t^{1/6}$.

The concentration of the titanium in the standard solution was determined gravimetrically and found to be 1×10^{-2} moles per liter as stated. The standard was diluted and checked by the peroxide colorimetric method (4). The calibration data obtained by plotting the diffusion current against the concentration are shown in Figure 1.

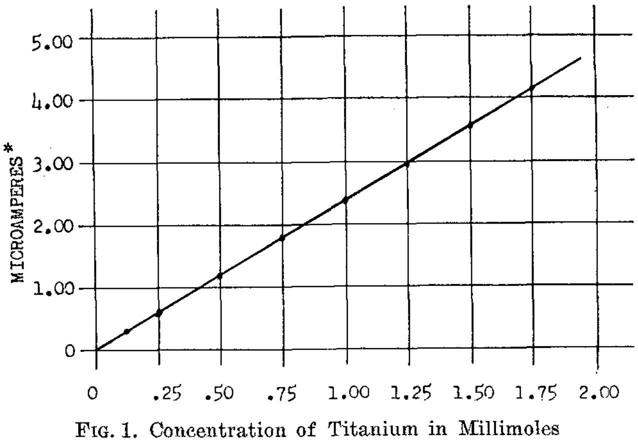

FIG. 1. Concentration of Titanium in Millimoles

* Corrected for residual current.

The above data were obtained by adding the required number of ml. of the standard solution to a 50-ml. volumetric flask, adding the correct amount of sulfuric acid to make 1.0 N, adding sodium oxalate to saturate, and making up to volume.

Method

Two grams of soap are weighed to ± .01 g. into a platinum crucible and burned with a low flame from a Bunsen burner until ashed. After the sample is ashed, 3 g. of potassium bisulfate are added, and again the crucible is heated with a low flame, preferably with a cover on, until the ash is completely fused. While the mass is in a fused condition, it is poured into a 100-ml. beaker and the crucible is likewise placed in the beaker. After the fused mass has cooled, 50 ml. of 1.0 N sulfuric acid are added and the beaker is heated slightly until the fused mass goes into solution. The contents of the beaker are then cooled and added to a 100-ml. volumetric flask, and the beaker and crucible are washed with a little 1.0 N sulfuric acid that is added to the flask, which is then made up to volume with 1.0 N sulfuric acid. A 25-ml. aliquot is added to a 50-ml. volumetric flask, to which sodium oxalate is added to make it saturated and 1.0 N sulfuric acid to make it up to volume. The sample is then placed in the electrolytic cell, and nitrogen is passed through the solution from 10 to 20 minutes to replace the air. The drop time was adjusted to give one drop in 3 to 6 seconds, and the polarogram was obtained between 0 to —.8 volts. The half wave potential *versus* the saturated Calomel Electrode was found to be —.240 ± .008 volts. An aliquot of the sample was also checked by the colorimetric method.

The results obtained from a number of soap samples from factory production and from pilot production are listed in Table I. These were made to correlate the exact amount of titanium added to that which was found. The titanium was converted to titanium dioxide and reported as such. The titanium was calculated from Figure 1 and also by using the Ilkovic equation (3). From the Ilkovic equation: $i_d = 605\, nD^{1/2}Cm^{2/3}t^{1/6}$ where i_d is the current in microamperes, n is the number of faradays of electricity required per mole of the electrode reaction, D is the diffusion co-efficient of the reducible or oxidizable substance in $cm.^2\ sec.^{-1}$, C is the concentration in millimoles, m is the rate of flow of mercury from the dropping electrode capillary expressed in $mg.\ sec.^{-1}$, and t is the drop time in seconds. There is, according to the Ilkovic equation, with all other factors constant, a linear relation between the diffusion current and concentration (3) $i_d = KC$. It is also shown that the diffusion current is a function of the rate of mercury flow and the drop time (3). With all other factors constant in the Ilkovic equation the diffusion current is found to be directly proportional to the product $m^{2/3}t^{1/6}$. $i_d = Km^{2/3}t^{1/6}$. In the Ilkovic equation the factors 605n and $D^{1/2}$ are constant and independent of the capillary whereas the diffusion current has been shown to be a function of the concentration and m and t which are determined experimentally. The factors 605 $nD^{1/2}$ are equal to $\frac{i_d}{Cm^{2/3}t^{1/6}}$ and are known as the diffusion current constant I. Thus the Ilkovic equation becomes $i_d = ICm^{2/3}t^{1/6}$. The diffusion current constant was determined experimentally from the following data: diffusion current 1.19, C = .50 millimoles, m = 1.8874 mg./sec. The time 3.33 sec. I = 1.2751 ± .003. The concentration of titanium was obtained from Figure 1, or calculated from the equation $C = \frac{i_d}{Im^{2/3}t^{1/6}}$. The diffusion current con-

TABLE I

Sample	Polarographically as TiO^2	Colorimetrically as TiO^2
1	0.062	0.062
2	0.062	0.062
3	0.130	0.132
4	0.187	0.187
5	0.250	0.250
6	0.312	0.312
7	0.365	0.365
8	0.431	0.431
9	0.063[a]	0.064
10	0.124[a]	0.125
11	0.187[a]	0.187

[a] Samples 9, 10, 11 were special pilot samples. These were made using 1,000 g. of soap, and C.P. Titanium Dioxide was added in the following ratio: .625 g., 1.25 g., and 1.875 g., respectively.

stant I serves two purposes. If the previously determined constant I and the factors m and t are known, it is possible to determine the concentration of the titanium without referring to a standard curve (2), and the I gives a means of correlating the diffusion currents, using different capillaries in the same electrolyte and at a known concentration when m and t are known (2).

Conclusion

Titanium dioxide can be determined in soaps polarographically by the method described above. It has been found that no maximum suppressor was necessary and that the diffusion current is directly proportional to the concentration and is well defined. The method is adaptable to soaps.

Acknowledgment

I wish to thank the Allen B. Wrisley Company, and Elmer R. Luckow for the time and consideration given me in working on this project.

REFERENCES

1. Adams, D. F., Titanium, Analytical Chemistry, *20*, 891 (1948).
2. Lingane, J. J., Ind. Eng. Chem., Anal. Ed., *15*, 583 (1943).
3. Kolthoff, L. M., and Lingane, J. J., "Polarography," New York, Interscience Publishers (1941).
4. Sandall, E. R., "Colorimetric Determination of Trace Metals," 423 New York, Interscience Publishers (1944).
5. Zeltzer, S., Collection Czechoslow., Chem. Commun., *4*, 319 (1932).

[Received January 21, 1954]

Letter to the Editor

DEAR EDITOR:

In the paper "The Composition of Coffee Oil and Its Component Fatty Acids" (J. Am. Oil Chemists' Soc., *30*, 606, 1953) the statement was made that "... previous work on coffee oil is meager ...".

The following references, dealing with oil of coffee grounds, contain much valuable data and interesting technological information:

R. INTONTI: Rendiconti dell'Ist. di Sanità Pubbl., March 1938.

M. TESTONI E G. BIMBI: La Chimica e l'Industria, *3*, 137 (1938).

G. B. MARTINENGHI: Oli Min., Grassi e Saponi, Col. e Vern., *18*(8), 113 (1938).

They may be of interest to your Journal readers.

GIOVANNI B. MARTINENGHI
PROFESSORE CORRISPONDENTE
DELL'ISTIT. NACIONAL DE OLEOS
DI RIO DE JANEIRO
Milano, Italy
March 22, 1954

ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor

The autoxidation of fats and application of antioxidants. H. Janecke (Univ. Frankfurt a. M., Germany). *Arzneimittel-Forsch.* 3, 574-86, 632-9(1953). A review.

Seed fats of cucurbits. D. K. Chowdhury, M. M. Chakrabarty, and B. K. Mukherji (Univ. Coll. Sci. Technol., Calcutta). *Science and Culture* (India) 19, 163-4(1953). Analysis of seeds and oils of *Cucurbita maxima, Benincasa cerifa, Lagenaria vulgaris,* and *Citrullus vulgaris* shows respectively: % oil, 48, 48.3, 45.1, 68.4; iodine value, 98.3, 126.8, 126.5, 116.2; component fatty acids as % by weight of the oil are: linoleic, 43.7, 62.3, 64.0, 58.6; oleic, 26.4, 21.9, 18.2, 18.7; saturated, 29.9, 15.8, 17.8, 22.7. (*C. A.* 48, 3708)

Confirming the erucic acid detection in oil mixtures by the oxidation method. H. Hadorn, R. Jungkunz, and K. W. Biefer (Lab. Berbandes Schweizerische Konsumvereine, Basel, Switzerland). *Z. Lebensm.-Untersuch. u. -Forsch.* 97, 365-73(1953). For detection of cruciferous-seed oils (rape, mustard) in olive, peanut, and other oils, the method of Kaufmann and Fiedler (*C. A.* 33, 419), based on $KMnO_4$ oxidation and isolation and identification of dihydroxybehenic acid, was found unsuitable. With a few modifications, principally increase in the $KMnO_4$ excess, sufficient improvement was obtained so that 10% admixtures of rapeseed oil to olive or peanut oils were detectable. (*C. A.* 48, 2393)

The stability of safflower-seed oil. M. N. Rao and M. Swaminathan (Central Food Technol. Research Inst., Mysore, India). *Bull. Central Food Technol. Research Inst.* 2, 211(1953). The seeds were minced, steamed 1 hr., and the oil expressed at 1.25 tons/sq. in.; the yield was 25%. Stability by the active oxygen method was 14.5 hrs. Safflower-seed oil was less stable than peanut oil in holding tests. The high content of glycerides of linoleic acid accounts for the low stability. (*C. A.* 48, 2393)

Melting and solidification of milk fat. H. Mulder (Agr. Univ., Wageningen, Holland). *Neth. Milk Dairy J.* 7, 149-74(1953). The expansion of solidified cream with 35% fat upon heating from 0 to 51° in van Dam's dilatometer is greatest in the region of 10-20°. The amount of fat which melts at a given temperature varies according to the temperature at which the cream was solidified. The lower the temperature at which the butter fat was caused to solidify the lower is its melting point. The thermal expansion of the liquid and of the solid fat at the same temperature is practically the same. The total expansion