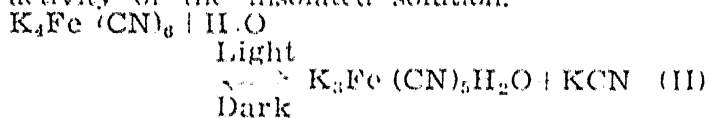


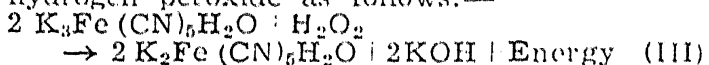
Such an equilibrium in the dark has also been postulated by Briggs.<sup>3</sup>

It is now suggested that on illumination of (I) the equilibrium is shifted far to the right, tending to set up a photostationary state, with increased concentration of potassium aquopentacyanoferrite, and consequently marked activity of the insolated solution.

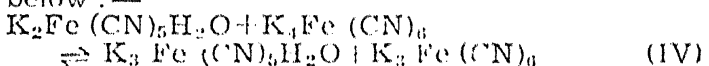


The aquo complex salt causes the photochemical after-effect. The reversion of (II) in the dark takes a measurable time, and thus explains the results shown in the last table.

Potassium aquopentacyanoferrite reacts with hydrogen peroxide as follows:—

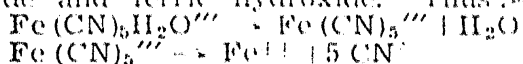


The primary oxidation process (III) is a highly exothermic reaction. This primary impulse may bring about the decomposition of a large number of hydrogen peroxide molecules by some yet unelucidated mechanism. The aquo-salt produced in (III) is reduced as below:—



Thus the stationary concentration of aquoferrite tends to be kept constant in presence of a large excess of ferrocyanide. The catalytic system  $Fe(CN)_5H_2O \rightleftharpoons Fe(CN)_5H_2O^+$  decomposes hydrogen peroxide at a high velocity, thus accounting for the marked photochemical after-effect.

It has been further observed that in aqueous solution, aquopentacyanoferrite undergoes a slow and complicated change on standing in the dark, finally producing ferrocyanide, ferricyanide and ferric hydroxide. Thus:—



This reaction is accelerated by heat and also by light, since aquopentacyanoferrite is photosensitive. In view of these changes, the behaviour of aged and heated solutions of ferrocyanide and the insolated solutions which are used sometime after darkening can be explained. Prolonged exposure of (II) results in the photo-decomposition of the aquo-salt, and the consequent lowering in its concentration. The maximum photochemical after-effect obtained with one minute's insolation and its subsequent diminution with prolonged insolation are thus to be expected.

Experimental evidence in support of these considerations has been adduced, and will form the subject of a separate communication.

The details of this investigation will appear elsewhere.

Chemical Laboratory,  
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## RESORCINOL-SUCCINEIN AS ADSORPTION INDICATOR IN ARGENTOMETRIC TITRATIONS

FOLLOWING the discovery of Fajans,<sup>1</sup> an intensive study has been made of phthaleins, sulphophthaleins and a few other dyes as adsorption indicators in precipitation reactions. Trials with resorcinol-succinein in argentometric titrations are described.

Two drops of the indicator (0.2 per cent. solution in alcohol) are sufficient for every 20 c.c. of the titration mixture. The following table shows the range of applicability of this indicator compared with Fluorescein in argentometry.

The new indicator, therefore, compares very favourably with fluorescein, and is definitely

Titration of	Fluorescein indicator (Titratable upto)	Resorcinol succinein (Titratable upto)
I <sup>-</sup>	N/100 (accuracy 0.5%)	N/4000 (accuracy 0.5%)
Br <sup>-</sup>	N/100	N/200
CNS <sup>-</sup>	N/100	N/100
Cl <sup>-</sup>	N/100	N/20

more sensitive for iodide ions, in which case solutions of N/4000 can be titrated.

Titration, as with other indicators of this class, are possible in neutral or just alkaline solutions but fail in acid solutions.

Chemical Laboratory, University of Allahabad, March 12, 1947.

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*I. Z. Electrochem.*, 1923, 29, 495.

## EFFECT OF STORAGE AND ACIDITY ON THE PROTECTION OF VITAMIN A IN SHARK LIVER OIL BY ANTI-OXIDANTS

IN an earlier communication,<sup>1</sup> it was reported that a combination of iso-butyl gallate and citric or tartaric acid affords a high degree of protection to vitamin A in fresh shark liver oil of low acid value (0.52), as judged by accelerated tests. The effect of antioxidants under normal storage conditions is reported here.

A sample of oil (B) of acid value 5.18, preserved in a refrigerator for about a year, was treated<sup>1</sup> with different concentrations of the antioxidants and stored at room temperature (18°-35° C.) in a number of ground-glass stoppered bottles (50 c.c.) painted black on the outside. The control oil as well as the treated oils were stored in triplicate. At regular intervals vitamin A was estimated<sup>2</sup> by the Carr-Price reaction using the Pulfrich Photometer with filter S. 61. The mean of the three values of each set is given in Table I.

Though the rates of fall of vitamin A are rather irregular, the beneficial effect of the antioxidants is obvious from the above table. In almost all the treated samples original

1. Ki-tiakowsky, W., *Zeit. Physikal. Chem.*, 1900, 35, 431. 2. Lal, B. B., *Jour. Ind. Chem. Soc.*, 1939, 16, 7, 321. 3. Briggs, S. H. C., *J.C.S.*, 1920, 117, 1029.

TABLE I

Period of storage in days	Vitamin A expressed as $\frac{100}{1 \text{ cm.}}$							
	Control oil	Oil with iso butyl gallate (G) and citric acid (C)						
		G (0.01%) C (0.005%)	G (0.02%) C (0.01%)	G (0.03%) C (0.015%)	G (0.04%) C (0.02%)	G (0.05%) C (0.025%)	G (0.06%) C (0.03%)	G (0.07%) C (0.035%)
0	6.86	6.86	6.86	6.86	6.86	6.86	6.86	6.86
30	6.21	—	—	—	—	—	—	—
60	5.39	—	—	—	—	—	—	—
120	4.44	6.86	6.86	6.86	—	—	—	—
180	3.74	"	"	"	—	—	—	—
240	3.22	6.44	"	"	6.86	—	—	—
300	2.86	6.05	6.51	"	"	6.86	—	—
360	2.58	5.44	5.83	6.95	6.27	6.27	6.47	6.47
420	2.34	4.51	5.08	5.17	5.18	5.39	5.61	5.68
480	2.27	3.63	4.18	4.46	4.76	4.76	5.09	4.41
540	—	3.10	3.54	3.24	4.34	4.36	4.44	4.46
600	—	2.75	3.02	3.02	3.07	4.17	4.11	4.17

vitamin A content was retained upto ten months, whereas in the control oil about 10 per cent. vitamin was lost after one month and about 60 per cent. within ten months. However, once the deterioration started in the fortified oils, it went on almost with the same speed as in the control. The effective concentration of the antioxidants for the highest protection appears to be 0.04 per cent. iso-butyl gallate + 0.02 per cent. citric acid.

Since commercial samples of pure shark liver oil are found to have acid values ranging from 0.5 to 20.0 (occasional samples having as high as 26.0), it was thought desirable to study the effectiveness of the antioxidants on oils of different acidities.

Samples of varying acid values, that were stored in the refrigerator upto the time of experiment, were dried<sup>3</sup> by filtering through a column of anhydrous sodium sulphate and treated<sup>1</sup> with and without antioxidants. 1 c.c. of each of the control and fortified oils was stored at 40° C. in bottles (50 c.c.) fitted with rubber stoppers and sealed with rosin wax. At regular intervals, three bottles of each set were taken out, the oils contained in them were mixed together and vitamin A was estimated as before. The induction periods were determined as reported in the previous communication.<sup>1</sup> The results are summarised in Table II.

In two cases, from about 2 gms. of an oil of low acidity, the fatty acids were isolated<sup>3</sup> and added to 25 gms. of the same sample of oil in order to demonstrate the influence of increased free acidity on the degree of protection afforded by the antioxidants to oils of the same origin but of different acidities.

The results show that high free acidity not only adversely affects the keeping quality of the unfortified oil, but also lowers considerably the efficiency of the added antioxidants. This observation is of obvious importance from the point of view of the commercial utility of antioxidants. Freshly extracted oils of low acid value only (preferably below 1.0) respond

to the action of the antioxidants studied. This again emphasises the importance of producing

TABLE II

Sample of oil	Acid value	Induction period (hours)		
		Control oil	Oil + Iso butyl Gallate (0.02%) + Citric acid (0.01%)	Oil + Iso butyl Gallate (0.01%)
A	0.54	68	1034	14.2
A + Acids	10.87	60	522	7.7
B	5.18	56	554	8.9
C	0.81	72	1116	14.5
C + Acids	12.02	62	528	7.5
D	2.95	58	644	10.1
E	1.32	64	826	11.9
F	0.98	68	1006	13.8
G	1.86	62	750	11.1
H	19.37	38	178	5.7
I	14.36	44	305	5.9

shark liver oil of very low acidity, which can only be achieved<sup>4</sup> by using fresh or well preserved livers.

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April 3, 1947.

S. M. Bose.

1. Bose, S. M., and Banerjee, B. N., *Ind. Jour. Med. Res.*, 1945, **33**, 203. 2. Dattatreya Rao, S., *Ibid.*, 1944, **32**, 165. 3. *Ibid.*, 1946, **34**, 91. 4. Dattatreya Rao, S., and Banerjee, B. N., *Ibid.*, 1944, **32**, 161.