

in which the ore samples were treated with sulfuric acid and salt cake.

The first method used involved selective extraction of the sulfates of barium and radium by boiling the concentrate with concentrated sulfuric acid (sp. gr. 1.82) whereby the bisulfates are formed; these remain in solution in an excess of the hot acid and are then removed by filtration followed by washing the insoluble residue with fresh portions of hot concentrated acid. From the combined filtrates the radium and barium are precipitated by dilution with 6 to 10 volumes of water containing a small quantity of barium chloride. After settling for 3 or 4 days, the diluted acid is run off and the sulfates collected on a filter. The crude sulfates thus obtained generally amounted to about 10 per cent of the concentrate taken; but it should be stated that the amount of crude sulfates obtained depends to a great degree upon the porosity of the filter used in filtering the hot acid liquors. We used for filters asbestos packed in a Buchner funnel, and plates of "Filtros" 4 cm. thick. Filtros plates of medium porosity allowed some of the fine sands to pass, thereby reducing the concentration to 4 or 5.

TABLE III—SECOND STAGE OF CONCENTRATING RADIUM

No.	Extraction with concentrated sulfuric acid	Fusion with mixed carbonates
1 Concentrate.....	50 g.	10 g.
2 Reagent used.....	183 g.	50 g.
3 Crude sulfates obtained.....	6.54 g.	0.596 g.
4 Radium in concentrate.....	5.60×10^{-6} g.	7.71×10^{-7}
5 Radium in crude sulfates.....	5.33×10^{-6} g.	8.42×10^{-7}
6 Radium recovered.....	95.18%	91.5%
7 Concentration ratio.....	7.64 : 1	16.8 : 1
8 Radium in tailings (film method).....	4.8%	1.0%
9 Radium in solutions.....	1.0%	1.0%

The results reported in Table III were obtained with asbestos filters and the finest grade of Filtros.

The second method of concentration tried was the customary procedure of decomposing silicates by fusion with mixed carbonates of sodium and potassium. When the fused mass was lixiviated with water, the soluble silicates were completely hydrolyzed. The insoluble residue, consisting of silica and the carbonates of radium and barium, was well washed with a 1 per cent solution of sodium carbonate until free from sulfates, and was then digested with dilute C. P. hydrochloric acid for several hours. After filtering and washing, a slight excess of sulfuric acid was added to the filtrate to precipitate the radium along with barium as sulfates. After standing for 4 days, to complete the precipitation of the sulfates, the liquid was run off and the precipitate collected on a filter. The solution of chlorides contained other bases in considerable quantity besides barium and radium, since the sulfates precipitated were found to weigh only one-third as much as the dry residue of chlorides. Typical experimental data obtained are given in Table III.

SUMMARY

I—A typical low-grade American carnotite was treated with concentrated sulfuric acid at elevated temperatures whereby radium and barium compounds are converted into bisulfates and the vanadium and uranium compounds are rendered soluble in water. From the resulting product a radium concentrate of fine sands was separated by lixiviating with a large volume of water followed by differential

sedimentation. Approximately 87 per cent of the radium was thus separated and practically all of the vanadium and uranium extracted. The concentration of radium in the sediment of fine sands ranged from 20 to 28 times that of the ore.

II—Low-grade carnotite when fused with sodium bisulfate or salt cake likewise yielded a product from which a radium concentrate was separated by treatment with water accompanied by differential sedimentation. The sediment of fine sand was found to carry approximately 86 per cent of the radium of the ore and its concentration was increased from 15 to 20 times, depending to some extent upon the purity of the salt cake used. Vanadium and uranium passed into solution nearly quantitatively.

III—Digestion of low-grade carnotite with sulfurous acid at room temperatures and differential sedimentation of the products resulted in a segregation of approximately 85 per cent of the radium in the finely divided gangue material at a concentration of 10 to 12 times that of the ore.

IV—The distribution of radium was determined among the solutions, concentrates, and residues obtained by the above methods of treating carnotites.

V—The radium in the concentrates obtained by treating the ore with sulfuric acid or salt cake was separated in the form of crude sulfates by two methods: (1) Digestion with an excess of concentrated sulfuric acid, and (2) fusion with mixed carbonates of sodium and potassium. The crude sulfates thus obtained contain fully 80 per cent of the radium of the ore, and the concentration ranges from 150 to 300 times that of the ore.

VI—Preliminary experiments were conducted on the extraction of radium from carnotites with chlorine water and carbonic acid.

VII—The radium content of the tailings obtained in treating the ore with sulfuric acid or salt cake when determined by the emanation method was found to exceed the values obtained by comparison of the radiation from equal areas of ore and tailings. Hence it is suggested that in the approximate determination of radium in such tailings by the latter method comparisons be made against standardized samples of tailings instead of ore.

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ERRORS IN THE DETERMINATION OF ACID VALUES OF BOILED OILS AND VARNISHES

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One of the most common analytical constants utilized in the valuation of fats, oils, and varnishes, is the neutralization or acid value. The procedure as outlined in standard texts is quite definite, although it is not ordinarily considered that any appreciable error is introduced by slight variations from recommended practice.

While it is well recognized that the regular pro-

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cedure is not satisfactory for the estimation of free fatty acids in alkali soaps, owing to the very decided hydrolysis of such materials in alcohol and ether, apparently no provision has been made for the occurrence of similar hydrolysis of the metallic soaps in the analysis of boiled oils and varnishes.

Ragg¹ does mention the hydrolysis of lead and zinc linoleates by water in discussing the perishability of paint films, but it has not generally been known that these soaps are similarly affected by alcohol.

While carrying out an investigation as to the rôle of metallic soaps in the deterioration of mixed paints during storage the authors were struck by the very evident hydrolysis of the metallic linoleates and resinates during the estimation of the free fatty acids in the vehicle of the aged paints under observation.

Since these salts of linseed oil are so easily hydrolyzed, it is apparent that their presence in the dissolved state would cause an oil to show an acid value which would include the amount of alkali necessary to hydrolyze the soaps present as driers as well as that required to neutralize the free fatty acids. This is a point which we believe has never before been brought to the attention of the oil chemists and is of great importance.

In order to study this influence that the metallic soaps exert on the determination of the acid value in oils, those soaps of linseed oil which are most likely to occur in a boiled oil or varnish, *i. e.*, lead, manganese, cobalt, calcium and zinc, were prepared by precipitation from a neutral solution of the sodium soap, and dried in a vacuum. Using 280 as the molecular weight of the acid radical, the theoretical acid numbers, assuming complete hydrolysis of KOH, were computed as follows:

LEAD	MANGANESE	COBALT	CALCIUM	ZINC
146.2	182.4	181.2	186.8	179.3

On titrating these soaps dissolved in an alcohol-ether mixture, the actual acid numbers found varied only a few tenths from the above figures, except in the case of calcium soap. This showed an acid number of but 79.5, indicating, as might have been expected, only partial hydrolysis. In these titrations the final end-point was taken when the pink of the phenolphthalein would remain for several hours without vanishing. However, the amount of alkali necessary after the first appearance of the fugitive pink color was in no case considerable.

The rosin salts of the same metals were prepared in a similar manner and dried in vacuum. On titrating these in an alcohol-ether solution, they gave the following results. The calculated acid value was computed from the formula $C_{20}H_{30}O_2$ for rosin:

	APPARENT ACID VALUE	CALCULATED ACID VALUE Assuming Complete Hydrolysis	Per cent Hydrolyzed
Lead salt.....	113.0	139.0	81.3
Manganese salt..	168.3	171.2	98.3
Cobalt salt.....	160.0	170.3	94.0
Calcium salt.....	86.0	175.3	49.1
Zinc salt.....	149.0	168.7	88.3

An oil having an original acid value of 3.05 was

heated with a quantity of lead linoleate to a slightly cloudy solution. This boiled oil had an ash content of 1.15 and an acid value of 10.20. A sample of the same oil run parallel to it but without the drier showed a final ash content of 0.18 per cent and an acid value of 2.31, the decrease in the latter value being due to the volatilization of some of the fatty acid originally present. The difference between the ash content of the oil containing drier and the oil without it indicated the presence of approximately one per cent of lead oxide in solution as the linoleate. This should cause an apparent acid number of 7.1 for the boiled oil, assuming hydrolysis to the same extent as in the previous experiments. The value of 10.20 actually found might indicate that the lead exerted some slight saponifying action on the oil at the high temperature employed in effecting the solution.

This error in the determination of the acid value of oils is in many cases not serious since the amount of soluble metallic soaps is limited. But in varnishes, where the hydrolyzable substance in solution is a metallic soap of rosin or gum, which may be present in considerable quantities, the apparent acid value is but a poor criterion of the conditions actually existing.

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STORAGE CHANGES IN VEGETABLE AND ANIMAL OILS

By HENRY A. GARDNER

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The writer's attention has recently been called to instances where linseed oil that has been separated from paints has shown low chemical constants. In one instance, several barrels of paint made of pure raw linseed oil stood in a factory yard for a few weeks, exposed in the daytime to the sun. A temperature of 115° F. was probably reached in the middle of the day. Upon analysis, the consumer found the oil that was separated from the paint to have a lower iodine number than that called for by the specifications. The shipment of paint was accordingly rejected. Since pure linseed oil of the proper iodine number was used in the paint, it is apparent that hydrolysis occurred on storage. That such changes are possible should, therefore, be considered by the testing engineer when examining the vehicles of specification paints that have not been freshly used or that have been exposed to high temperatures during storage.

The writer has previously pointed out the degree of change which may be expected to take place in linseed oil when ground with various pigments,¹ and he has also indicated the contributing effects of impurities in oils.² Some more recent work has shown that nearly all oils, even when not in contact with pigments, will show changes in their chemical constants when allowed to stand for a period of time. The drop in iodine number is generally accompanied by a rise in specific gravity and acid value.

Quantities of a number of oils were obtained by

¹ The "Effect of Pigments upon the Constants of Linseed Oil," H. A. Gardner, *J. Frank. Inst.*, Oct., 1912, pp. 415-423.

² "Changes Occurring in Oils and Paste Paints, Due to Autohydrolysis of the Glycerides," H. A. Gardner, *J. Frank. Inst.*, May, 1914, pp. 533-540.

¹ *Oesterr. Chem.-Ztg.*, [2] 12, 62-4.