

precipitates of the lead sulfate type, such as barium sulfate, lead arsenate, lead chromate, etc. The determination is made right in the precipitation beaker or flask, and the procedure is of such simplicity that the authors feel the method may be of considerable use in the estimation of small amounts of many substances.

The technique used in the formation of these "spots" was as follows. The liquid in the flask was first swirled twenty or thirty times, to loosen the precipitate and cause part of it to go to the center. Then after allowing the precipitate to settle for a minute or two, the flask was tipped so that the line made by the edge of the liquid crept nearly to the center of the flask bottom. Sufficient liquid was present in the flask so that the flask bottom made a maximum angle of about  $60^\circ$  with the desk top. This was done ten times to the left, ten times to the right, and ten times each backward and forward. The precipitate was brought to the center of the flask bottom by this procedure.

Finally the flask was held by the thumb and finger of the right hand near the bottom and the thumb and finger of the left hand near the top, over a black surface. The right hand now made a series of short backward and forward movements (about ten to a series, at the rate of three or four a second). During these movements the flask did not move more than a millimeter or two, and the force was applied by the whole forearm, the wrist being held practically stiff. After each series of shakes the flask was rotated  $30$  or  $40^\circ$ . These vibrational movements caused the precipitate to be swept into a compact circular pile. Photographs of spots obtained are given in Fig. 1.



0.01 Mg. 0.12 Mg. 0.17 Mg. 0.27 Mg. 0.63 Mg.  
Fig. 1.—Lead sulfate "spots."

After a few minutes of such shaking the spot reached an essentially constant, minimum size. The flask was then placed on the "standard spot" card (Fig. 2) and moved along until a spot was reached which matched the unknown spot in size. This card was simply a reduced copy of a contact photograph of a twist drill and steel wire gage. It was calibrated with known amounts of precipitate. A sheet of millimeter graph paper can be substituted for occasional determinations.

This vibration method was used to obtain circles having an apparent area up to about twenty square millimeters. For larger amounts than this the minimum area of the square was obtained by the tipping process described above. The dimensions of the square could be rapidly obtained by placing the flask on millimeter graph paper.

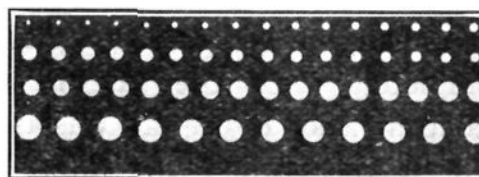


Fig. 2.

Quantitative results are given in Table I for lead sulfate in contact with 10 cc. of 40% sulfuric acid, measured in a 50-cc. Pyrex Erlenmeyer flask.

TABLE I					
Mg. lead present	Mg. lead found	Impurities present, mg.	Mg. lead present	Mg. lead found	Impurities present, mg.
0.08	0.08	None	0.06	0.08	Sn (10)
.20	.19	None	.10	.13 <sup>a</sup>	As (10) Bi (1)
.13	.14	None	.20	.19 <sup>a</sup>	Cu (10) Cd (1)
.10	.09	None	.30	.32 <sup>a</sup>	As (1) Bi (1) Cu (1)
.04	.06	None			Sb (1) Sn (1)
.02	.03	None	.40	.37 <sup>a</sup>	Cu (1) Cd (1)
.04	.05	None	.50	.54 <sup>a</sup>	Cu (10) Cd (10)
.20	.15	Cd (10)	1.0	1.3 <sup>a</sup>	As (10) Bi (10)
.12	.10	Cu (50)			Cu (10)
.09	.10	Bi (10)	2.0	1.8 <sup>a</sup>	Cu (5) Cd (5)
.08	.08	Bi (50)	3.0	2.7 <sup>a</sup>	As (5) Sb (10)
.06	.12	As (50)			Sn (10)
.17	.18	Sb (10)	4.0	4.2 <sup>a</sup>	Cu (4) Cd (4)

<sup>a</sup> Precipitate washed three times, redissolved and reprecipitated.

MORLEY CHEMICAL LABORATORY  
WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO

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### The Catalytic Oxidation of Carbon

BY JESSE E. DAY,<sup>1</sup> RICHARD F. ROBEY AND HYP J. DAUBEN

A few years ago, Taylor<sup>2</sup> reported a means of demonstrating the peculiar catalytic effect of sodium chloride on the oxidation of soot carbon, a phenomenon well known to the layman in its practical application.

We have successfully performed the demonstration of Taylor many times; it was discovered, however, that not only sodium chloride is effec-

(1) Because of the untimely death of Professor Jesse E. Day, on April 19, 1935, the junior authors have been deprived of the benefits of his kindly guidance and criticism in the preparation of this paper.—R. F. R. and H. J. D.

(2) R. K. Taylor, *THIS JOURNAL*, **52**, 3025 (1930).

tive, but other salts apparently equally as well. This seemed so striking that we immediately endeavored to verify this observation in a somewhat more exact manner.

A small tube (2.4 cm. in diameter) was rotated (3 r. p. m.) on its long axis inside a split type laboratory combustion furnace. A short (4 cm.) length of the tube, in the center of the furnace, and having a negligible temperature gradient, was coated completely with the salt in question. Thus the concentration of the salt was assumed to be constant at the carbon-salt interface. The temperature of the furnace was then increased to and maintained at a predetermined convenient value ( $\pm 3^\circ$ ). Carbon film deposition, mirror reflected observation, and air admittance were made through a narrow longitudinal slot (2 cm. wide) in the under portion of the surrounding furnace. The apparatus was entirely enclosed in a small glass-fronted cabinet to protect it from drafts.

Carbon deposition was carried out by means of a wide flame of enriched natural gas from a Pyrex glass burner which moved mechanically along the slot in the furnace at a uniform rate (0.02 cm./sec.). The flame deposited the carbon film uniformly, as evidenced by the manner in which it disappeared on oxidation, and at a rate of 3.5 micromoles/sec., reproducible within 10%.

The lengths of time required for the disappearance of the carbon film from the 4 cm. sector were determined when deposited on bare glass as well as on the following c. p. salts: lithium, sodium, potassium, calcium, strontium and barium chlorides, calcium and barium hydroxides, sodium and potassium sulfates.

At  $575^\circ$  the carbon burned off the bare glass in about 180 sec. This was cut down by all of the salts to between 20 and 30 sec., as far as could be discerned by the method of observation. At  $550^\circ$  the oxidation of the carbon from the bare surface required 280 sec. It was reduced by the presence of the salts to 130-150 sec. At  $515^\circ$ , the oxidation from the bare surface required 630 sec. This was cut down by the barium and strontium salts to about 300, by the calcium salts and sodium chloride to about 230, and by the potassium and lithium chlorides, and sodium and potassium sulfates to about 170 sec. The values given are the averages of two or more observations usually agreeing within 10% or less. This agreement evidences a fair reproducibility of oxidizable surface area.

The most ready explanation of the effect of salts in the oxidation of carbon is that offered by Taylor and Neville.<sup>3</sup> They pointed out that the probable function of salts in the reaction of steam on carbon is in hastening the decomposition of the  $C_xO_y$  surface complex. With this barrier removed, a carbon surface is more readily attacked by oxidizing gases.

(3) H. S. Taylor and H. A. Neville, *THIS JOURNAL*, **43**, 2055 (1921).

CHEMICAL LABORATORY  
THE OHIO STATE UNIVERSITY  
COLUMBUS, OHIO

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### The Isolation and Identification of a Paraffin Hydrocarbon from Urine of Pregnancy

BY WILLIAM FERRIS HART AND M. ALLEN NORTHP

Marrion<sup>1</sup> has mentioned that a paraffin hydrocarbon which is physiologically inactive, occurs in urine of pregnancy. Schwenk<sup>2</sup> also states that he has encountered a physiologically inactive hydrocarbon in urine of pregnancy.

We have isolated and identified one hydrocarbon, heptacosane, from urine of pregnancy, and have evidence of the presence of another, pentacosane, in the same material.

**Experimental.**—Twelve liters of urine were aged for several months and acidified to Congo red with concentrated hydrochloric acid, the acidified urine was then treated with 28 g. of fuller's earth per liter, agitated thoroughly, and allowed to stand overnight. The fuller's earth was then filtered off, and a second absorption on 14 g. per liter was applied. The combined fuller's earth fractions were air dried and extracted seven times with convenient volumes of low boiling petroleum ether (below  $70^\circ$ ). The combined petroleum ether residue was taken up in 50 cc. of ethyl acetate. This solution, on chilling, deposited 1.4 g. of white plate-like crystals. It was found on recrystallizing from methanol that this material could be separated into two fractions, one soluble, and the other insoluble, in warm methanol.

The fraction insoluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was  $58-59^\circ$  (uncorrected). Analysis gave: C, 85.83 and 84.56, H, 14.62 and 14.62; molecular weight (micro Rast), 391, 391. Calcd. for heptacosane ( $C_{27}H_{56}$ ): C, 85.16,

(1) Marrion, *Physiol. Rev.*, **13**, 185 (1933).

(2) E. Schwenk, private communication.