# Identification of Organic Compounds by Use of Chromium Target X-Ray Diffraction Powder Patterns

F. W. MATTHEWS AND J. H. MICHELL

Canadian Industries Limited, Central Research Laboratory, McMasterville, Quebec

### X-RAY APPARATUS AND TECHNIQUE

A study was made of the x-ray diffraction powder diagrams of a series of solid derivatives (anilides) of saturated aliphatic acids. It has been found that the use of chromium target x-radiation gives patterns of increased dispersion with the result that each member of the homologous series C1 to C18 can readily be distinguished and identified. Structural isomers within the series may also be identified. Technical details on the use of chromium radiation for powder diffraction work are described. Tables of powder diffraction measurements are given.

HE use of x-ray diffraction patterns for the identification of crystalline material was outlined by Hull (10) in 1919 when he showed that a crystalline substance gives a diffraction pattern which is always the same for the same substance, and is sufficiently different from many of its chemical homologs to enable identification to be made. The application of the method has been mainly confined to inorganic compounds and minerals; the number of crystalline organic compounds recorded is relatively small. Of the one thousand patterns listed by Hanawalt, Rinn, and Frevel (9), forty-nine are of organic compounds. This is due in part to the complex nature of the powder patterns resulting from crystals of comparatively low symmetry. This condition should be improved if greater dispersion of the pattern were accomplished by the use of radiation of longer wave length and/or larger camera diameter and necessary refinement of collimator design. These difficulties were discussed at a recent meeting in England on the subject of physical methods of identification of materials, reported by Bannister (2). At this meeting Bunn suggested the use of larger camera diameter to give greater pattern dispersion.

The use of x-ray powder diffraction patterns for the identification of organic compounds poses certain unique problems. For example, the success or failure of the method in identifying individual members of a homologous series will depend upon the extent to which an additional methylene group affects the powder pattern of a typical member of the series. The differences between the patterns for each adjacent member must be sufficiently clear to establish identification. Similarly, the patterns for structural isomers must be distinctive. Rodgers (2) reported

that in almost all cases powder patterns have proved exact enough to discriminate unambiguously between different organic compounds, even those of essentially similar chemical structure.

Recent work by McKinley, Nickels, and Sidhu on the identification of phenols (13) and by Clarke, Kaye, and Parks (5) on the identification of aldehydes and ketones by means of x-ray diffraction powder patterns clearly showed the applicability of the method. No published powder data, however, were available with which to evaluate the ability of the method to distinguish between each member of a homologous series, or of a number of structural isomers.

For the present work, the anilides of the saturated aliphatic acids were chosen. The identity of the anilides could readily be checked, as ample melting point data were available (11). These same anilides have been investigated by Robertson (16) for the purpose of relating melting point and molecular structure.

General Electric XRD Type I diffraction equipment was used in recording the powder patterns. Increased pattern dispersion was accomplished by the use of chromium  $K-\alpha$  ( $\lambda = 2.285 \ kX$ ) radiation. The effect on pattern dispersion of this longer waveradiation. The effect on pattern dispersion of this longer wave-length radiation is illustrated in Figure 1. A very marked im-provement in pattern dispersion and definition will be seen in the change from molybdenum  $K-\alpha$  ( $\lambda = 0.708 \ kX$ ) and copper  $K-\alpha$ ( $\chi = 1.537 \ kX$ ). The same pattern dispersion could be accomplished by the use of larger camera diameters but the refinement in the collimator system required to give suitable definition of the pattern, together with the increased target to specimen and specimen to film distances, would require longer exposure times. The source of chromium radiation was a General Electric CA-6 Coolidge type tube with beryllium metal windows. The use of beryllium metal as the window of the tube is reported by Atlee (1) to give greatly increased useful intensity for wave length of x-radiation larger than 1.5 kX.

The filter used to pass essentially the K- $\alpha$  wave length was Amend, New York, N. Y.) ground in cellulose acetate or nitrate cement (14). (Duco Household cement was found very satis-factory.) The mixture was thinned with amyl acetate and spread on glass to give a uniform film. After evaporation of the solvent, the film was stripped from the glass plate under water. The concentration found to give satisfactory removal of the Cr  $K-\beta$  lines was 15 mg, of vanadium pentoxide per square centimeter. This figure was determined by a series of powder photographs of sodium chloride taken with a range of concentrations of vana-dium pentoxide in the filter. The concentration at which the (200) reflection due to  $K-\beta$  was barely detectable was considered satisfactory. The powder camera used was that of the General Electric XRD unit, the diameter being 143.2 mm. The specimen was mounted in a wedge, which was adjusted in the camera by sighting through the pinhole collimator to intercept one half of the beam. The tube was operated at a potential of 35 kv. and a current of 15 ma. Using Eastman Type K radiographic film the exposure time required was about 4 hours.

The relative intensities of the lines of the powder diffraction pattern should refer to randomly oriented powders. In the case of organic compounds which crystallize in needles or plates, this condition is experimentally difficult to obtain particularly in the case of wedge specimen mounts. The samples used were carefully ground in an agate mortar. In the case of one particularly ground in an agate mortar. In the case of one particularly plate-like material, propionanilide, a second sample was ground with Pyrex. No significant variation in relative line intensity was noted when compared to the previous photograph. The Pyrex adds considerably to the absorption in the specimen.



Figure 1. X-Ray Powder Diffraction Patterns of Acetanilide

Effect of change of x-ray wave length on pattern dispersion and resolution Top. Mo K- $\alpha$  radiation,  $\lambda = 0.71 \ kX$ Middle. Cu K- $\alpha$ ,  $\lambda = 1.54 \ kX$ Bottom. Chromium radiation,  $\lambda = 2.29 \ kX$ Camera diameter 143.2 mm.

Table I.	Melting	Points of	Anilides	of /	Aliphatic	Acids
----------	---------	-----------	----------	------	-----------	-------

Acid	No. of Carbon Atoms in Acid	Melting Point, °C. (This Research)	Melting Point, ° C. (11)
Formie Acetic Propionic n-Butyric Isobutyric n-Valeric Isovaleric Garvic Hivalic n-Caproic Isocaproic Enanthic Caprylic Pelargonic Capric Undecylic Lauric Myristic Palmitic Stearic	$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       4 \\       5 \\       5 \\       5 \\       5 \\       5 \\       5 \\       5 \\       6 \\       6 \\       7 \\       8 \\       9 \\       10 \\       11 \\       12 \\       14 \\       18 \\     \end{array} $	$\begin{array}{c} 47.6\\ 113.6\\ 104\\ 93.5\\ 102.5\\ 63\\ 109\\ 109\\ 132\\ 94.5\\ 111\\ 64\\ 54\\ 57.5\\ 68\\ 70\\ 78\\ 85\\ 91\\ 95\\ \end{array}$	$\begin{array}{c} 50\\ 114.1\\ 104-104.5, 105.6\\ 92, 96, 97\\ 104-105, 105\\ 61-62, 62-63, 63\\ 109, 5, 109-110, 110\\ 105, 5-106.5, 108, 110-111\\ 128, 132-133\\ 92, 94-5, 96\\ 110.5, 111.5, 112\\ 64, 65, 69\\ 55, 57\\ 57\\ 70\\ 71\\ 76, 5, 78\\ 80-82, 84\\ 90.5, 90.6\\ 94, 95, 5\end{array}$

Lindemann glass or beryllium metal powder might give improved results.

#### PREPARATION OF ANILIDES

Formanilide was prepared by boiling an equimolar mixture of 87% formic acid and aniline until the temperature of the mixture reached 280° C. (18). The product was recrystallized from low-boiling petroleum ether. By refluxing together equimolar quantities of the acid and freshly distilled aniline for 2 to 3 hours the following anilides were prepared: acetanilide (19), propionanilide ( $\beta$ ), *n*-butyranilide, isobutyranilide, *a*-methylbutyranilide, pivalanilide, and caproanilide (12). The anilides of *n*-valeric, isovaleric, and isocaproic acids were prepared (7) by adding aniline to a benzene solution of the corresponding acid chloride in the proportion of 2 moles of aniline to 1 of acid chloride. In each case the mixture was brought to gentle reflux for 10 minutes, then cooled, and the aniline hydrochloride removed by filtration. Evaporation of the filtrate gave the crude crystalline anilide. In the same way the anilides of undecylic, lauric (4), myristic, palmitic (7), and stearie acids were prepared (8). The anilides of enanthic, caprylic, plargonic, and capric acids were obtained by heating equimolar proportions of the acid and aniline in sealed tubes at a temperature of 160° to 190° C. for 2 hours (15). In general it was found that the anilides of lower members of the series (C<sub>2</sub> to C<sub>5</sub>) could be crystallized readily from ethanolwater mixtures, the intermediate members (C<sub>6</sub> to C<sub>11</sub>) could be crystallized from petroleum ether, and the higher members (C<sub>12</sub> to C<sub>18</sub>) could be crystallized from benzene.

The melting points of the prepared anilides, as well as the values given in the literature, are given in Table I.

#### DISCUSSION OF POWDER DIFFRACTION DATA

The powder diffraction data for the anilides of the normal aliphatic acids from  $C_1$  to  $C_{12}$ , inclusive, and of the even-numbered carbon acids  $C_{14}$  to  $C_{18}$  as well as for the iso acids  $C_4$ ,  $C_6$ , and  $C_6$  and of two other structural isomers of the  $C_5$  aliphatic acid are listed in Table II (p. 664). The intensities recorded were estimated from a visual examination of the film. The most intense lines of the patterns are listed in Table III and in Table IV the compounds are listed in order of the strongest line of the patterns.

Examination of the powder diffraction data for unique characteristics by which identity of the compounds can be established shows that the patterns of the anilides of the normal acids  $C_1$  to  $C_8$  are readily distinguished. The patterns of the even numbers of the series  $C_8$  to  $C_{18}$  show a marked similarity, suggesting a uniformity of crystal structure which may be described as "isostructural". Each pattern, however, has unique characteristics by which it can be distinguished; this is particularly true of the longest *d* spacing recorded, which shows a measurable stepwise change with increasing chain length of the acid. Only two acids with an odd number of carbon atoms greater than  $C_8$  were examined. These indicated that a separate isostructural series is formed by these compounds. These results are in agreement with the findings of Slagle and Ott (17) in their x-ray investigation of the fatty acids.

A graphic representation of the melting point vs. carbon chain length of the compounds as given by Robertson (17) (see Figure 2) shows no regular relationship up to C<sub>8</sub>. From C<sub>8</sub> to C<sub>18</sub> the data show regularly increasing melting points with increasing carbon chain length. This result is in conformity with the isostructural relationship found in the examination of the powder data.

The effect of structural isomerism on the powder diffraction pattern was examined in the case of the normal and isoisomers of butyric, valeric, and caproic acids. The pattern of the straightchain derivative could be readily distinguished from that of its structural isomer. In the case of the  $C_b$  acid four structural isomers were examined: *n*-valeric, isovaleric,  $\alpha$ -methylbutyric, and pivalic acids. The diffraction patterns of the anilides of these acids could be readily distinguished.

Since the x-ray diffraction powder pattern is specific for each polymorphic form of a substance, the possible existence of such forms should be considered. From the x-ray diffraction examination no evidence was observed of polymorphic changes in these compounds. All samples were crystallized from solvents, at room temperature. These conditions would tend to give a product stable at room temperature. Patterns taken at intervals of several months on the same specimen showed no change. The

Table III. Four Strongest Lines of Powder Diffraction Patterns of Anilides of Some Saturated Aliphatic Acids

Name	No. of Carbon Atoms in Aliphatic . Acid	1st Line	2nd Line	3rd Line	4th Line
Formanilide Acetanilide Propionanilide n-Butyranilide Isobutyranilide Isobutyranilide Isovaleranilide d.l-a-Methylbutyr- anilide	1 2 3 4 4 5 5 5 5	$\begin{array}{c} 3.61 \\ 9.44 \\ 3.75 \\ 4.05 \\ 7.09 \\ 4.77 \\ 7.41 \\ 7.28 \end{array}$	$\begin{array}{c} 3.75 \\ 5.92 \\ 6.17 \\ 5.05 \\ 4.05 \\ 3.64 \\ 4.13 \\ 4.17 \end{array}$	3.09 3.64 8.59 5.65 5.72 10.25 9.95 3.28	5.163.414.463.554.475.505.005.17
Pivalanilide n-Caproanilide Isocaproanilide Enanthanilide Caprylanilide Pelargonanilide Capranilide Undecylanilide Lauranilide Myristanilide Stearanilide	5 6 7 8 9 10 11 12 14 16 18	$\begin{array}{c} 7.14\\ 3.82\\ 4.21\\ 4.70\\ 16.4\\ 17.0\\ 19.1\\ 4.05\\ 3.86\\ 4.36\\ 4.40\\ 4.41\end{array}$	$\begin{array}{c} 4 & 20 \\ 3 & 55 \\ 7 & 51 \\ 4 & 15 \\ 4 & 03 \\ 8 & 46 \\ 4 & 25 \\ 20 & 7 \\ 3 & 85 \\ 3 & 85 \\ 3 & 85 \end{array}$	$\begin{array}{c} 4 & 62 \\ 5 & 55 \\ 4 & 80 \\ 4 & 00 \\ 3 & 94 \\ 4 & 49 \\ 9 & 12 \\ 3 & 64 \\ 3 & 75 \\ 11 & 6 \\ 3 & 75 \\ 3 & 74 \end{array}$	5.00 4.77 3.53 3.78 8.06 3.95 3.93 17.4 3.61 3.73 3.63 3.65

Table IV. Data Arranged in Order of Strongest Line of Diffraction Pattern

1st Line	2nd Line	3rd Line	4th Line	No. of Carbon Atoms in Aliphatic Acid	Name
$\begin{array}{c} 3.61\\ 3.75\\ 3.92\\ 3.86\\ 4.05\\ 4.05\\ 4.36\\ 4.41\\ 4.70\\ 4.77\\ 7.14\\ 7.28\\ \end{array}$	$\begin{array}{c} 3.75\\ 6.17\\ 3.55\\ 20.7\\ 5.05\\ 4.25\\ 7.51\\ 3.855\\ 3.855\\ 4.15\\ 3.64\\ 4.020\\ 4.17\end{array}$	$\begin{array}{c} 3.09\\ 8.59\\ 5.55\\ 3.75\\ 5.65\\ 3.64\\ 4.80\\ 11.6\\ 3.75\\ 3.74\\ 4.00\\ 10.25\\ 5.72\\ 4.62\\ 3.28\end{array}$	$\begin{array}{c} 5,15\\ 4,46\\ 4,77\\ 3,61\\ 3,55\\ 17,4\\ 3,73\\ 3,63\\ 3,73\\ 3,63\\ 3,78\\ 5,50\\ 4,47\\ 5,00\\ 5,17\\ \end{array}$	$     \begin{array}{r}       1 \\       3 \\       6 \\       12 \\       4 \\       11 \\       6 \\       14 \\       16 \\       18 \\       7 \\       5 \\       4 \\       5 \\$	Formanilide Propionanilide n-Caproanilide Lauranilide Undecylanilide Isocaproanilide Myristanilide Palmitanilide Enanthanilide r-Valeranilide Isobutyranilide d./-a-Methylbu- tyranilide
7.41 9.44 16.4 17.0 19.1	$\begin{array}{r} 4.13 \\ 5.92 \\ 4.03 \\ 8.46 \\ 4.05 \end{array}$	9.953.663.944.499.12	5.00 3.41 8.06 3.95 3.93	5 2 8 9 10	Isovaleranilide Acetanilide Caprylanilide Pelargonanilide Capranilide

Vol.	18,	No.	11
------	-----	-----	----

				Ta	ble II. X	(-Ray I	Diffraction	Data	-				
Formani d	lide, Cı $I/I_1$	Acetani d	lide, C2 <i>I/I</i> 1	Propionan d	ilide, C <sub>3</sub> $I/I_1$		n-Capros (Con d	ntd.)	Isocapros (Cor d	anilide, Cs ntd.) I/I	1	Enantha (Cont d	nilide, $C_{1}$ td.)
$14.0 \\ 7.28 \\ 7.03 \\ 6.19 \\ 5.61 \\ 5.61 \\ 5.32 \\ 6.4 \\ .86 \\ 4.86 \\ 4.33 \\ 4.13 \\ 3.75 \\ 3.61 \\ 3.52 \\ 3.45 \\ 3.61 \\ 3.52 \\ 3.45 \\ 3.09 \\ 2.93 \\ 2.93 \\ 2.81 \\ 2.65 \\ 1.6 \\ $	$\begin{array}{c} 0.50\\ 0.15\\ 0.20\\ 0.20\\ 0.05\\ 0.10\\ 0.25\\ 0.40\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.10\\ 0.50\\ 0.80\\ 1.00\\ 0.02\\ 0.05\\ 0.40\\ 0.80\\ 0.05\\ 0.15\\ 0.15\\ 0.55\\ \end{array}$	$\begin{array}{c} 9.\ 44\\ 6.\ 66\\ 6.\ 33\\ 5.\ 92\\ 5.\ 09\\ 4.\ 83\\ 4.\ 67\\ 4.\ 40\\ 4.\ 23\\ 4.\ 03\\ 3.\ 95\\ 3.\ 86\\ 3.\ 58\\ 3.\ 66\\ 3.\ 58\\ 3.\ 41\\ 3.\ 26\\ 3.\ 17\\ 3.\ 02\\ 2.\ 79\\ 2.\ 74\\ 2.\ 65\\ \end{array}$	$\begin{array}{c} 1 & 00 \\ 0 & 505 \\ 0 & 050 \\ 0 & 500 \\ 0 & 500 \\ 0 & 500 \\ 0 & 050 \\ 0 & 050 \\ 0 & 000 \\ $		$\begin{array}{c} 0.\ 60\\ 0.\ 80\\ 0.\ 40\\ 0.\ 60\\ 1.\ 00\\ 0.\ 60\\ 0.\ 10\\ 0.\ 10\\ 0.\ 10\\ 0.\ 05\\ 0.\ 10\\ 0.\ 05\\ 0.\ 10\\ 0.\ 05\\ 0.\ 10\\ 0.\ 05\\ 0.\ 10\\ 0.\ 05\\ \end{array}$		3.55 3.46 3.22 2.98 2.89 2.51 2.45 2.17 2.04	0.80 0.10 0.10 0.10 0.10 0.10 0.10 0.10	3.80 3.53 3.45 3.31 2.93 2.89 2.83 2.78 2.72 2.56 2.53 2.45 2.25 2.25 2.19 2.13 1.99 1.94 1.91	$\begin{array}{c} 0.10\\ 0.50\\ 0.10\\ 0.50\\ 0.15\\ 0.02\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.05\\ 0.10\\ 0.05\\ 0.10\\ 0.15\\ 0.10\\ 0.15\\ 0.05\\$		2.00 .78 .59 .27 2.27 2.21	0.80 0.80 0.60 0.10
2,55 2,52 2,38 2,34 2,30 2,24 2,18 2,04 2,01	$\begin{array}{c} 0.05\\$	2.56 2.46 2.42 2.38 2.35 2.25 2.19 2.16 2.04 2.01 1.93 1.90	$\begin{array}{c} 0.15\\ 0.15\\ 0.10\\ 0.05\\ 0.20\\ 0.20\\ 0.20\\ 0.05\\ 0.10\\$				n-Capryla 16.4 12.9 11.1 10.2 8.06 6.65 5.59 4.77 4.38 4.22 4.03 3.94	nilide, Ce 1.00 0.20 0.20 0.20 0.20 0.10 0.20 0.10 0.20 0.20 0.20 0.60 0.60 0.60	Pelargona 17.0 11.5 10.6 8.46 5.92 4.49 4.40 4.25 4.05 3.95 3.78 3.68 3.68	nilide, Cs 1.00 0.10 0.80 0.20 0.50 0.20 0.10 0.40 0.50 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.00 0.20 0.10 0.20 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.10 0.00 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.10 0.20 0.50 0.20 0.50 0.20 0.05	C 19 16 10 10 10 10 10 10 10 10 10 10 10 10 10	apranili 1 1 1 2 4 3 4 4 4 4 4 4 4 4 4 4 4 4 4	de, C <sub>10</sub> 1.00 0.02 0.10 0.05 0.80 0.15 0.30 0.50 1.00 0.60 0.40
$\begin{array}{c} n\text{-Butyran} \\ 10.25 \\ 8.64 \\ 7.73 \\ 6.94 \\ 5.65 \\ 5.05 \\ 4.78 \\ 4.67 \\ 4.45 \end{array}$	ilide, C4 0.05 0.05 0.05 0.05 0.30 0.50 0.10 0.10 0.7	Isobutyra 9.94 7.09 5.72 5.00 4.77 4.47 4.20 4.05 3.86	nilide, C4 0.40 1.00 0.60 0.50 0.50 0.60 0.60 0.10 0.80 0.20	$\begin{array}{c} d, l-\alpha \cdot \mathrm{Methylbut} \\ 10, 27 \\ 7, 28 \\ 6, 58 \\ 5, 80 \\ 5, 17 \\ 4, 93 \\ 4, 77 \\ 4, 63 \\ 4, 55 \end{array}$	tyranilide, 0.20 1.00 0.05 0.60 0.70 0.30 0.30 0.70 0.20	Cs	3.66 3.22 3.14 3.06 2.89 2.57 2.39 2.10 Undecylar	0.20 0.05 0.15 0.10 0.05 0.05 0.05 0.05 0.0	2.05 Lauranili	0.15 0.15	M	. 50 . 14 . 98 yristanil	0.10 0.30 0.10
4 05 3 92 3 73 3 47 3 35 3 09 3 00 2 64 2 47 2 04	1.00 0.15 0.15 0.30 0.30 0.20 0.07 0.02 0.05 0.10	3.62 3.47 3.35 3.18 3.11 2.99 2.29 2.25 2.05	$\begin{array}{c} 0.05\\ 0.02\\ 0.30\\ 0.20\\ 0.15\\ 0.02\\ 0.05\\ 0.05\\ 0.07\\ \end{array}$	$\begin{array}{c} 4.46\\ 4.33\\ 4.17\\ 3.95\\ 3.70\\ 3.43\\ 3.28\\ 3.12\\ 3.01\\ 2.95\\ 2.89\\ 2.71\\ 2.61\\ 2.33\\ 2.22\\ 2.33\\ 2.20\\ 2.09\end{array}$	$\begin{array}{c} 0.05\\ 0.05\\ 1.00\\ 0.30\\ 0.80\\ 0.80\\ 0.40\\ 0.15\\ 0.10\\ 0.15\\ 0.10\\ 0.15\\ 0.05\\ 0.10\\ 0.15\\ 0.05\\ 0.10\\ 0.15\\ 0.05\\ 0.10\\ 0.15\\ 0.05\\ 0.10\\ 0.10\\ 0.15\\ 0.05\\ 0.10\\ 0.05\\ 0.10\\ 0.05\\ 0.10\\ 0.05\\ 0.05\\ 0.10\\ 0.05\\ 0.05\\ 0.10\\ 0.05\\ 0.05\\ 0.10\\ 0.05\\$		d 17.4 8.89 5.98 4.66 4.25 4.05 3.64 3.42 3.29 3.21 3.14 3.02 2.81	$\begin{array}{c} I/I_1 \\ 0.20 \\ 0.20 \\ 0.15 \\ 0.05 \\ 0.05 \\ 0.50 \\ 1.00 \\ 0.20 \\ 0.50 \\ 1.00 \\ 0.20 \\ 0.30 \\ 0.15 \\ 0.02 \\ 0.015 \\ 0.02 \\ 0.05 \\ $	$\begin{matrix} d \\ 20.7 \\ 10.30 \\ 9.27 \\ 8.13 \\ 6.94 \\ 5.37 \\ 4.52 \\ 4.38 \\ 4.05 \\ 3.86 \\ 3.75 \\ 3.81 \\ 4.05 \\ 3.81 \\ 3.14 \\ 3.07 \\ 2.33 \\ 2.30 \end{matrix}$	$\begin{array}{c} I/I_1 \\ 0.60 \\ 0.15 \\ 0.30 \\ 0.30 \\ 0.02 \\ 0.15 \\ 0.10 \\ 0.40 \\ 0.30 \\ 1.00 \\ 0.50 \\ 0.50 \\ 0.20 \\ 0.05 \\ 0.05 \end{array}$	212 11 12 6 6 6 4 4 4 4	d 	$1/l_1$ 0.30 0.50 0.50 0.30 0.30 0.30 0.30 0.20 0.30 0.40 1.00 0.50 0.50 0.50 0.20 0.20 0.20 0.50 0.20 0.
Isovaleran d	ilide, C <sub>5</sub> $I/I_1$	n-Valerani d	lide, C <sub>6</sub> $I/I_1$	Pivalanili d	de, C5 <i>I/I</i> 1		$2.45 \\ 2.35 \\ 2.30 \\ 2.29$	0.02 0.02 0.02			2 2 2	.31 .18	$0.10 \\ 0.05 \\ 0.02$
$\begin{array}{c} 9.95 \\ 7.41 \\ 7.00 \\ 5.85 \\ 5.00 \\ 4.75 \\ 4.59 \\ 4.13 \\ 3.88 \end{array}$	$\begin{array}{c} 0.80\\ 1.00\\ 0.02\\ 0.50\\ 0.70\\ 0.70\\ 0.05\\ 1.00\\ 0.20\\ \end{array}$	$\begin{array}{c} 10.25 \\ 6.48 \\ 5.50 \\ 5.25 \\ 4.77 \\ 4.59 \\ 4.44 \\ 4.25 \\ 3.78 \end{array}$	$\begin{array}{c} 0.60 \\ 0.50 \\ 0.60 \\ 1.00 \\ 0.05 \\ 0.05 \\ 0.10 \\ 0.10 \\ 0.15 \end{array}$	$\begin{array}{c} 7.14\\ 6.10\\ 5.83\\ 5.21\\ 5.00\\ 4.62\\ 4.51\\ 4.41\\ 4.20\\ \end{array}$	$1.00 \\ 0.01 \\ 0.20 \\ 0.50 \\ 0.60 \\ 0.30 \\ 0.15 \\ 1.00 \\ 0.01 \\ 0.01 \\ 0.00 \\ $		2.24 2.18 2.07 2.04 2.00	0.05 0.05 0.02 0.05 0.05 Palmitan d	ilide, $C_{15}$ $I/I_1$		Stearan d	ilide, Cu	I I I
3.70 3.47 3.34 3.19 3.07 2.45 2.29 2.11 2.04	$\begin{array}{c} 0.20\\ 0.70\\ 0.70\\ 0.20\\ 0.30\\ 0.05\\ 0.05\\ 0.05\\ 0.10\\ 0.10\\ \end{array}$	3.64 3.50 3.39 3.33 3.00 2.88 2.38 2.04	1.00 0.20 0.30 0.10 0.05 0.05 0.10 0.10	$\begin{array}{c} 4.04\\ 3.37\\ 3.29\\ 3.13\\ 2.98\\ 2.91\\ 2.85\\ 2.74\\ 2.65\\ 2.74\\ 2.65\\ 2.44\\ 2.39\\ 2.33\\ 2.26\\ 2.23\end{array}$	$\begin{array}{c} 0.10\\ 0.20\\ 0.20\\ 0.10\\ 0.02\\ 0.05\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.02\\ 0.05\\ 0.02\\$	•		12.610.39.128.217.346.555.314.864.564.234.234.134.003.85	0.50 0.10 0.02 0.30 0.15 0.15 0.20 0.05 1.00 0.05 1.00 0.05 1.00 0.05 0.15 0.05		$\begin{array}{c} 16.4 \\ 14.0 \\ 12.2 \\ 10.9 \\ 9.49 \\ 8.78 \\ 7.79 \\ 7.09 \\ 6.75 \\ 5.74 \\ 5.25 \\ 4.81 \\ 4.41 \\ 4.01 \\ 2.85 \end{array}$		20 20 22 22 25 55 22 22 22 22 22 21 21 21 21 21 20 20 20 20 20 20 20 20 20 20 20 20 20
n-Caproar d 10.8 7.57 6.85 5.92 5.85 4.77 4.67 4.31 3.82	$\begin{array}{c} \text{iilide, } C_{8} \\ I/I_{1} \\ 0.15 \\ 0.05 \\ 0.20 \\ 0.05 \\ 0.60 \\ 0.60 \\ 0.10 \\ 0.10 \\ 1.00 \end{array}$	$\begin{matrix} \text{Isocaproar} \\ d \\ 14.8 \\ 7.51 \\ 5.92 \\ 5.59 \\ 5.16 \\ 4.80 \\ 4.36 \\ 4.21 \\ 4.05 \end{matrix}$	$\begin{array}{c} \text{iilide, } C_{6} \\ I/I_{1} \\ 0.20 \\ 0.80 \\ 0.30 \\ 0.05 \\ 0.30 \\ 0.80 \\ 0.30 \\ 1.00 \\ 0.10 \end{array}$	Enanthan d 8.13 7.21 5.88 5.79 5.59 5.59 5.16 4.70 4.47 4.15	ilide, $C_7$ $I/I_1$ 0.20 0.30 0.60 0.10 0.10 0.02 1.00 0.02 0.80			5.63 3.14 3.06 2.42 2.35 2.30 2.11 2.07 2.04	0.00 0.10 0.02 0.02 0.05 0.02 0.02 0.02 0.02		3, 74 3, 65 3, 14 2, 43 2, 08 2, 05		50 50 50 50 50 50 50 50 50 50 50 50 50 5

•



optical studies of Bryant (3) on the *p*-bromoanilides of the aliphatic acids showed metastable polymorphic forms which, however, were evident only in crystallizations from melt.

It was noted that extreme purity of the crystalline samples was not necessary in obtaining distinctive diffraction patterns. For instance, a crude sample of acetanilide, melting 5° below that of National Bureau of Standards microanalytical acetanilide, gave a pattern identical with that of the purer sample. This is an indication that great care in recrystallizing a derivative until a constant melting point is reached may not always be necessary for identifications when the x-ray diffraction method is employed. This observation is in agreement with the authors' experience in the wider application of the method.

#### SUMMARY

Using chromium target x-radiation, the powder diffraction patterns for the anilides of the normal saturated fatty acids ( $C_1$ to  $C_{18}$ ) were shown to be sufficiently characteristic to enable individual identification. The anilides of structural isomers of several of the fatty acids gave distinctive diffraction patterns. Extreme purity of the crystalline derivatives was found to be unnecessary in obtaining characteristic patterns.

## LITERATURE CITED

- (1) Atlee, J. Z., Gen. Elec. Rev., 46, 233 (1943).
- (2) Bannister, F. A., J. Sci. Instruments, 23, 34 (1946); Nature, 157, 234 (1946)
- (3) Bryant, W. M. D., and Mitchell, J., J. Am. Chem. Soc., 60, 2748 (1938).
- (4) Caspari, C. E., Am. Chem. J., 27, 305 (1902).
- (5) Clarke, G. L., Kaye, W. I., and Parks, T. D., IND. ENG. CHEM., ANAL. ED., 18, 310 (1946).
- (6) Crossley, A. W., and Perkin, W. H., Jr., J. Chem. Soc., 73, 33 (1898)
- Fournier, M. H., Bull. soc. chim. (4), 7, 25, 26 (1910). (7)
- (8)Guy, J. B., and Smith, J. C., J. Chem. Soc., 1939, 615.
- (9) Hanawalt, J. D., Rinn, H. W., and Frevel, L. K., IND. ENG. CHEM., ANAL. ED., 10, 457 (1938).
- (10) Hull, A. W., J. Am. Chem. Soc., 41, 1168 (1919).
- (11) Huntress, E. H., "Identification of Pure Organic Compounds", Order I, New York, John Wiley & Sons, 1941.
- Kahrs, E., Z. Krist., 40, 491 (1905).
- (13) McKinley, J. B., Nickels, J. E., and Sidhu, S. S., IND. ENG. CHEM., ANAL. ED., 16, 303 (1944).
- (14) Reynolds, D. H., Monsanto Chemical Co., Dayton, Ohio, private communication.
- Robertson, P. W., J. Chem. Soc., 93, 1033 (1908). (15)
- (16) Ibid., 115, 1210 (1919).
- (17) Slagle, F. B., and Ott, E., J. Am. Chem. Soc., 55, 4396 (1933).
- Wallach, O., and Wüsten, M., Ber., 16, 145 (1883).
   Williams, C. G., J. Chem. Soc., 17, 106 (1864).

# Determination of Hydrogen Sulfide in Gases

EDMUND FIELD AND C. S. OLDACH<sup>1</sup>

Ammonia Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

Two colorimetric methods have been developed for the analysis of traces of hydrogen sulfide in gases. The hydrogen sulfide is first absorbed in a caustic solution, and in the more sensitive method is converted to bismuth sulfide. The concentration of the resulting suspension is determined by means of a spectrophotometric measurement. In the absence of a spectrophotometer the sulfide is made to

**THE** sensitivity of even the elaborate titration technique described by Shaw (3) for the determination of hydrogen sulfide is inadequate for such special applications as the study of catalyst poisons, particularly where the lack of sensitivity cannot conveniently be overcome by increasing the size of the sample to be analyzed. In a more effective procedure for the determination of traces of hydrogen sulfide, presented by Moses and Jilk (2), a photoelectric cell measures the degree of darkening of a lead acetate-impregnated tape through which the gases are passed. The present paper describes another approach to the problem whereby as little as 1.4 micrograms of hydrogen sulfide in aqueous solution can be detected optically. Two procedures were developed specifically to meet the problems of the identification and determination of organic sulfur compounds present as impu-

<sup>1</sup> Present address, Belle, W. Va.

react with a uranyl-cadmium reagent and analyzed by visual comparison in a chromometer. With the spectrophotometric method as little as 7 micrograms of hydrogen sulfide may be determined with a precision of  $\pm 10\%$ . For larger samples the precision improves to  $\pm 3\%$ . The chromometer technique requires five times as much sulfide for equal precision, but still is far more sensitive than titration.

rities in commercial gases and solvents. Their application to the solution of these problems will be described in succeeding papers.

Both of the analytical methods described employ a solution of the hydrogen sulfide in 6% aqueous sodium hydroxide. For the applications under consideration this involves scrubbing the sulfide-bearing gas with caustic. In the more sensitive of the two analytical methods the sulfide in solution is converted to bismuth sulfide and the concentration of the resulting suspension is determined by measuring the transmission of monochromatic light with a spectrophotometer. The precision of the analysis is determined by the amount of hydrogen sulfide collected in the absorbing solution. The precision is  $\pm 10\%$  when 7 micrograms of hydrogen sulfide are collected. This corresponds to the amount of sulfur in 0.1 cubic foot of gas containing sulfur in a concentration of 0.11 grain per 100 cubic feet (1 grain per 100 cubic feet = 22.9micrograms per liter). With larger concentrations of sulfur or a larger sample, a precision of  $\pm 3\%$  can be achieved.