MICRO-IDENTIFICATION OF ISOMERS AND HOMOLOGUES IN THEIR MIXTURE.

I. THREE ISOMERIC XYLENES.(1)

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Xylene occurs more or less in almost every sample of petroleum. In coal-tar it is one of the chief constituents of the " solvent naphtha ", and it is contained also in raw wood-spirit. Thus xylene is very often met with in

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(1) More detailed description shall be given in the Nippon Kwagaku Kwaishi in Japanese.

studies of hydrocarbons, yet satisfactory methods to identify its three isomers, *o*-, *m*- and *p*-xylenes, especially in a sample of limited quantity, could not be found in literature.

It would be proper to consider that xylene, obtained by dry distillation of natural products, is a decomposition product of more complicated substances. If we can ascertain to which of three isomers the xylene in question belongs, it would enable us to get a key to trace its origin in the mother substances. For this purpose, I have tried to detect and identify three isomeric xylenes in their mixture with the smallest quantity of the sample. Two methods, sensitive colour-reaction and observation under microscope, were tried for identification in micro-scale.

I. Colour-reaction.

Among phenomena such as oxidation, reduction, halochromy, pseudomerism, etc., which produce colour-change, pseudomerism seems to have the widest application in analytical field. Nitro-compounds often give sharp colour-reactions when they are transformed from nitro- to aci-form; detection of primary and secondary alcohols by V. Meyer's method and Liebermann's reaction for secondary amines are good examples of application of pseudomerism of nitro-derivatives.

On the colour-reactions of nitro-derivatives of aromatic hydrocarbons, Stultz⁽¹⁾ describes that alcoholic solution of trinitro-pseudo-cumene gives with a drop of caustic potash an intense green coloration which turns brown after a short time. Trinitro-*m*-xylene gives under the same condition similar colour-reaction, while 2, 4-dinitro-toluene produces a pure blue colour and 2, 4, 6-trinitro-toluene a fuchsine red. On the other hand, no colour change is observed in the case of 2, 6-dinitro-toluene and trinitro-mesitylene.

Lepsius⁽²⁾ describes also that 2, 4, 6-trinitro-toluene gives in acetone solution a bordeaux red coloration.

As no description is found about trinitro-*p*-xylene, I have prepared from pure *m*- and *p*-xylenes their trinitro-derivatives (2, 4, 6-trinitro-*m*-xylene and 2, 3, 5-trinitro-*p*-xylene), and examined their colour-reactions towards alkali in some solvents.⁽³⁾

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(1) *Ber.*, **42** (1909), 3608.

(2) *Chem. Zt.*, **20** (1896), 839.

(3) As for *o*-xylene, it is known for its stability toward nitrating agent, and under the same condition in which *m*- and *p*-xylenes form trinitro-derivatives, it only forms oily lower nitro-compounds.

1. **Alcoholic solution.** With a drop of caustic potash, the *m*-compound in this solution gives instantly an intense bluish green coloration which turns on standing dull yellow, and finally a dark brown precipitate settles from the solution. In the case of the *p*-compound colour does not develop instantly, but in a few second the solution is tinged orange and then turns to a reddish brown tone, similar to that of iodine-tincture. On standing, the solution becomes turbid and a reddish brown deposit appears.

Thus we can observe remarkable differences in the two colour-reactions: (1) The colours produced by the two components form a fair contrast. (2) Both colorations do not occur simultaneously; one takes place instantly, while the other after a sufficient interval. (3) In the first the coloration fades in its tone while in the second it becomes deeper in the course of time.

From these facts we can expect that these reactions may be highly sensitive when applied to the detection of *m*- and *p*-xylenes in their mixture. In fact, when a mixture of the two alcoholic solutions above mentioned is treated with a drop of alkali, bluish green coloration appears at once, and after a short time, the reddish colour, characteristic to trinitro-*p*-xylene, predominates. The tinge of the first coloration and the time-required for appearance of the second, are variable with different proportions of the two components. The larger the quantity of the *m*-compound is, the more intense is the green coloration and the longer is the time required. For example, light green colour, which is immediately followed by the second coloration, is distinctly observed with a mixture of 2 c.c. of alcoholic solution of the *p*-compound and 0.05 c.c. of that of the *m*-compound. According to Blanksma⁽¹⁾ 100 c.c. alcohol dissolves 0.039 gr. trinitro-*m*-xylene at 20°C., consequently only 0.00002 gr. of the *m*-compound is contained in 0.05 c.c. of the alcoholic solution. The above example serves to show the sensitivity of this colour-reaction.

2. **Acetone solution.** The colours produced by the trinitro-*m*- and *p*-xylenes in this solution, with a drop of caustic alkali, are dark green and reddish brown respectively, and both colorations take place instantly, and do not change rapidly in their tones. Therefore, in case of mixture, a mixed colour is observed. For example, an acetone solution containing two trinitro-compounds in about equal proportion, takes a violet hue. On the other hand, in a mixture very rich in one of the components, the colour produced by the other can hardly be distinguished. Therefore, this reaction

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(1) *Rec. trav. chim.*, 25 (1906), 177.

appears, at first sight, to be of no value for analytical purpose. Nevertheless, this colour-reaction is indispensable to detect and identify the very small quantity of *p*-xylene in a mixture rich in *m*-xylene; for acetone dissolves, even when hot, only a trace of trinitro-*m*-xylene but readily the *p*-compound. On the other hand, as the two nitro-compounds are almost equally soluble in alcohol, if the identification of the same sample is carried out in alcoholic solution, the colour produced by the *p*-compound will be ambiguous.

In conclusion, in the case of a mixture of pure isomeric xylenes we can successfully detect and identify *m*- and *p*-xylenes by colour-reactions of their trinitro-compounds either in alcoholic or in acetone solution.(1) But in the case of a mixture with other compounds, as is often the case, say in solvent naphtha, substances with similar colour-reactions, such as trinitro-pseudo-cumene, 2, 4-di- und 2, 4, 6-trinitro-toluene must be previously removed. This will be an easy task if we avail the small solubility of triniro-*m*- and -*p*-xylenes in ordinary solvents, such as ether, alcohol, and acetone.

II. Microscopic Method.

An application of a polarisation microscope for identification of a very minute quantity of substances has already been recommended by Emich,(2) Behrens,(3) and others. In case of mixture, however, it is applicable only under the following conditions: (1) Crystals to be examined should be of different optical properties. (2) Crystals of each component should be roughly separated by some suitable solvents. This condition is necessary to raise accuracy and sensitivity of the result.

Besides, when refractive indices of a crystalline organic compound are measured by immersion-method, it must be kept in mind that organic substances, different from inorganic ones, are more or less soluble in immersion-media. And as this always causes the change of refractive indices of the media, we can not often find the true values for refractive indices of organic substances. For analytical purpose, however, accurate values for refractive indices are not necessary, and it is sufficient to find a medium which stands, with regard to refractivity, in different relations with each component of the mixture in question.

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(1) Actual treatments shall be described in a later paper.

(2) Emich, "Lehrbuch der Mikrochemie", 2 Aufl. (1926), 21.

(3) Behrens-Kley, "Mikrochemische Analyse", I, 4 Aufl. (1921); "Organische Mikrochemische Analyse", 2 Aufl. (1922).

Now, to detect the three isomers of xylene under microscope, we must first obtain their crystalline derivatives. As a simple and effective method for this purpose, so-called "direct substitution" processes, nitration, bromination, and sulphonation, were tried.

1. **Esotetrabromo-compounds.** Among various brominated xylenes, esotetrabromo-xylenes are the most preferrable for its easiness of formation and for having no isomers. Properties important for distinction of the three esotetrabromo-xylenes are given in Table 1.

TABLE 1.

	Esotetrabromo-*o*-xylene.	Esotetrabromo-*m*-xylene.	Esotetrabromo-*p*-xylene.
Melting point.	258°*	240°**	253°
Solubility.	Soluble in hot $CHCl_3$; sparingly in cold.	Soluble in cold $CHCl_3$; soluble in hot acetone.	A little soluble in cold $CHCl_3$; sparingly in hot acetone.
Properties of crystals.	White silky needles; extinction straight; elongation negative.	The same.	The same.
For Aniline.	$n_1 > N$.***	n_1 slightly $> N$.	$n_1 > N$.
For α-Br-$C_{19}H_7$ and CH_2I_2.	A little soluble. $n_2 > 1.8$.****	Readily soluble. The same.	Readily soluble. The same.

* Values reported by different observers are not same: 261° (Klages and Sommer), 254–5° (Blümlein), 260° (Jacobsen).

** 240° (Fittig and Bieber), 247° (Auwers and Krieckritz).

*** n_1 and n_2 are indices of the faster and the slower rays in a crystal respectively. Therefore, always $n_1 < n_2$. In this report N represents refractive index of the medium in question, but is not always equal to that of the pure medium.

**** As the consequence of having 4 atoms of Br in one molecule, these compounds have such extremely high refractive indices, that n_2 cannot be measured with ordinary immersion-media. This is a drawback of these compounds.

Though we have solvents to separate the three tetrabromo-compounds, their optical properties, as shown in the table, are insufficient to distinguish them. In short, they are not proper derivatives to identify three isomeric xylenes under microscope.

2. **Trinitro-compounds.** *o*-Xylene is difficulty nitrated, trinitro-*p*-xylene can not have any isomer structurally. Only *m*-xylene is capable to form three isomeric trinitro-derivatives, but as the consequence of the orienting influence of the two meta-standing methyl- and of added nitro-groups, 2, 4, 6-trinitro-*m*-xylene is the only product obtained by the direct substitution with nitrating acid. Here again, the trinitro-compounds are rather easily prepared than the lower ones. Some properties of trinitro-*m*- and -*p*-xylenes are shown in Table 2.

TABLE 2.

	2,4, 6-Trinitro-*m*-xylene.	2,3,5-Trinitro-*p*-xylene.
Melting point.	179°*	137–8°
Solubility.	Very sparingly soluble in alcohol and acetone, both in hot and cold.	Very sparingly soluble in hot and cold alcohol; soluble in hot acetone.
Crystalline form, etc.,	Thin prisms or hexagonal plates, with beautiful interference colour; pale yellow.	Thick prisms; light yellow.
Optical properties.	Extinction straight; elongation positive.**	Extinction straight;*** elongation negative.
For α-Br-$C_{10}H_7$.	$n_1 < N < n_2$ (for prisms); $n_2 \fallingdotseq N$ (for plates).	$n_1 > N$.

* Here again, values given by different observers are not concordant 176° (Grevingk), 177° (Luhmann), 180–1° (Knoevenagel), 182° (Tilden).

** Freshly formed crystals have elongations both positive and negative, but crystals recrystallised from alcohol have only positive elongation.

*** Trinitro-*p*-xylene crystallises in monoclinic prisms, but the cleavage being perfect toward (001), the face most frequently observed is (001) [Groth, "Chemische Krystallographie," IV, 667]. Hence nearly all crystals extinct in straight position. Very few crystals show oblique extinction. Their angle of extinction amounts about 30° [28° (Groth)].

As it is evident from the above table, the trinitro-compounds are most satisfactory derivatives for the identification of *m*- and *p*-xylenes.(1) Their refractive indices need not be measured. We are only to determine their signs of elongation. However, it is better to make sure of the result by determining the refractive indices.

3. Sodium salts of the sulphonic acids. Trinitro-derivatives leave little to be desired for the detection of *m*- and *p*-xylenes. But as we have not a suitable method to detect *o*-xylene, finally sulpho-derivatives were examined.

o-Xylene easily forms 4-sulphonic acid when treated with conc. sulphuric acid at 80–90°C.(2) Under the same condition *m*-xylene forms 4- and 2-sulphonic acids, but the former in far larger quantity.(2) *p*-Xylene-sulphonic acid is usually obtained by dissolving *p*-xylene in weak fuming sulphuric acid,(2) and one of the technical methods to separate *p*-xylene is based on its insolubleness in ordinary conc. sulphuric acid. However, I have observed that under the above condition, it is also easily converted into 2-sulphonic acid, as Crafts(3) has already mentioned.

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(1) A sample, very rich in *m*- or *p*-xylene, can be determined simply from the observation of its nitration. When a sample is very rich in *p*-xylene, dinitro-*p*-xylenes separate out as a crystalline mass, during or after the addition of nitrating acid. In the case of a sample containing a large quantity of *m*-xylene, trinitro-*m*-xylene crystallises out in beautiful long needles from the reacting mixture, when heated in an oil bath.

(2) Jacobsen, *Ber.*, **10** (1877), 1009; **11** (1878), 22.

(3) *Z. anal. Chem.*, **32** (1893), 243.

For the purpose of identification under microscope, their barium salts were first compared. Solubility in water markedly decreases in the order of *m*-, *o*-, and *p*-derivatives, but they proved unsuitable for analytical purpose, for *o*- and *m*-compounds only form crystalline crusts, without giving well-defined crystals.

The sodium salts were next prepared from the barium salts, and their properties compared (see Table 3).

TABLE 3.

	Na *o*-xylene-4-sulphonate.	Na *m*-xylene-4-sulphonate.	Na *p*-xylene-2-sulphonate.
Solubility.	Not readily soluble in H_2O; soluble in hot alcohol, not readily in cold.	Soluble in H_2O; soluble in alcohol.	Not readily soluble in H_2O; a little soluble in hot alcohol; sparingly in cold.
Crystalline form.	Prisms or flat needles.	Well-defined rhombic plates.	Prisms or flat needles.
Optical properties.	Extinction straight; elongation positive.	} The same.	The same.
For cedar oil	$n_1 < N$.	$n_1 \gtreqless N$.	$n_1 > N$.
For $C_2H_4Br_2$	$n_1 < N < n_2$.	$n_1 < N < n_2$.	$N < n_1 < n_2$.

The crystals of sodium sulphonate of *p*-xylene are distinguished from its isomers by its refractive indices. But the *o*- and *m*-compounds cannot be distinguished by this way, the only key in this case being their crystalline forms. The *m*-compound when slowly crystallises out from alcohol, forms well-defined rhombic plates, the two internal angles of which are about 80° and 100° respectively, while the *o*-compound crystallises in prisms or in flat needles. Consequently *o*-compound is detected by finding prismatic crystals whose smaller refractive index is lower than that of cedar oil.

It must be here added, however, that, as the crystalline forms of the salts of these sulphonic acids seem to have tendency to be easily disturbed by the presence of their isomers, we cannot expect the results of this method to be highly sensitive.

An Actual Example.

All the above mentioned methods were tested with various mixtures and proved to be applicable. An example of the analysis of commercial xylene shall be briefly described.

"Xylol" on market was distilled with Hempel's still-head, and two fractions, 135–8°C. and 140–2°C. were taken.

Detection of *m*- and *p*-xylenes. To 1 c.c. of the first fraction, 10 c.c. of the nitrating acid(1) (conc. H_2SO_4 1 : fuming HNO_3 2) were slowly added under water tap. The mixture was then heated in an oil bath at 110–120°C. for an hour, and the content was poured into water. The raw product was purified by washing with ether, and by recrystallising from a large amount of alcohol. Then the detection of isomeric xylenes in the sample was carried out in two ways.

By colour-reaction. When one portion of crystals thus obtained was tested in alcoholic solution with KOH, the intense green coloration instantly occurred. (Presence of *m*-xylene!) Next, the other portion was treated with hot acetone, when the greater part remained undissolved. (This shows that the sample was very rich in *m*-xylene.) The acetone solution gave the red coloration with KOH. (Presence of *p*-xylene!)

By microscopic method. Crystals, which remained undissolved in hot acetone, were examined under microscope; they had straight extinction and positive elongation, and their refractive indices stood in the following relation: $n_1 < \alpha$-bromonaphthalene $< n_2$. These crystals are nothing but trinitro-*m*-xylene. On the other hand, those separating out from acetone solution on cooling were found to be a mixture of two crystals, one of which was of positive elongation and the other negative, and the mixture contained the latter in far larger quantity. Those crystals with positive elongation proved to be trinitro-*m*-xylene from their refractive indices, and those of negative elongation were ascertained to be trinitro-*p*-xylene, for both of their refractive indices were greater than that of α-bromonaphthalene.

Detection of *o*-xylene. When 1 c.c. of the second fraction was shaken with equal volume of conc. H_2SO_4 at 80–90°C. for 30 minutes, nearly all the sample was absorbed in the acid. The sulphonic acids were converted into Ba salts in usual way, and from their aqueous solution two fractions of crystals were obtained. Dissolving each fraction in hot water, Ba was precipitated with a_2NCO_3. The filtrate was evaporated to dryness, and the sodium sulphonates were extracted with hot alcohol.(2) Crystals separating out from the somewhat concentrated alcoholic solution were not well-defined, and found in an aggregate state. Few prismatic crystals were found, but they proved to be the *p*-compound by their refractive indices. None of the crystals had properties of the *o*-compound, thus proving its absence.

To make sure, another c.c. of the second fraction was brominated with an excess of bromine in the presence of reduced iron. The product after

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(1) An excess of nitrating acid must be added, otherwise, *p*-xylene forms only dinitro-derivatives which are readily soluble in ether.

(2) Sodium sulphonates were also prepared directly by dropping the mixture of the raw sulphonic acids with excess of conc. H_2SO_4, in 4 times its volume of saturated NaCl solution.

washing with alkali and HCl successively, was several times recrystallised from chloroform, collecting every time crystals separating out first. Long white needles finally obtained melted at 252–3°C., which is exactly the m. p. of the pure esotetrabromo-*p*-xylene.

Thus in the commercial xylene in question no appreciable quantity of *o*-xylene was detected.

Appendix.

As the above mentioned principle,(1) on which one of the technical methods of separating *p*-xylene from its isomers is based, seems to be very doubtful, I have re-examined the method.

Five hundred c.c. of the commercial xylene, same as that used in the above experiments, was shaken with equal volume of conc. H_2SO_4 for 30 min., and the unabsorbed portion, which was only few percent of the sample, was fractionated. The first drop distilled at 145°C., and the thermometer rapidly rose to 160°C., while the b. p. of *p*-xylene is 135–6°C. Here, we can conclude that nearly all *p*-xylene was absorbed in sulphuric acid, consequently this technical method is not recommendable for that purpose.

Summary.

Methods to detect and identify the three isomeric xylenes in their mixture, especially in limited quantity, are given.

1. *m*-Xylene and *p*-xylene, even in minute quantity, can be successfully identified as their trinitro-derivatives, by their colour-reactions in alcoholic or acetone solution toward alkali, or by the optical properties of their crystals. These two methods leave little to be desired.
2. *o*-Xylene is identified microscopically as sodium sulphonate, but in case of a mixture very poor in *o*-xylene, we can not expect a result of high sensitivity by this method.
3. The technical method to separate *p*-xylene from its isomers, based on its insolubility in ordinary conc. sulphuric acid, is tested and shown to be of little value.

In conclusion, I must express my hearty thanks to Dr. I. Okada for his kind help in practical treatment of the microscope.

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(1) See p.196.