atomic ratio 1:1. These compounds had been prepared by precipitating water solutions of Me^{4+} perchlorates with the equivalent of "cupferron" ($= \text{NH}_4\text{C}_6\text{H}_8\text{N}_2\text{O}_8$), dissolving the compounds obtained, preferably in chloroform, and slowly evaporating the solutions. The crystals were light yellow for $\text{Me} = \text{Zr}^{4+}$, light yellowish brown for $\text{Me} = (\text{Zr}, \text{Hf})^{4+}$ and light brown for $\text{Me} = \text{Hf}^{4+}$. They were all rather long rods with a rhombic cross-section.

From single crystal photographs of $\text{Zr}(\text{C}_6\text{H}_5\text{N}_2\text{O}_8)_4$ (hkl - $hk7$, $h0l$ - $h5l$, $0kl$ - $8kl$) taken in Weissenberg cameras with CuK radiation, it was concluded that it is orthorhombic with the following dimensions:

$$\begin{aligned} a &= 16.7 \pm 0.2 \text{ \AA} \\ b &= 11.2 \pm 0.1 \text{ \AA} \\ c &= 14.4 \pm 0.2 \text{ \AA} \\ V &= 2.69 \cdot 10^3 \text{ \AA}^3 \end{aligned}$$

From a few Weissenberg photographs of the (Zr, Hf) and Hf compounds, it was found that the three compounds are isomorphous and that their cell dimensions, within the experimental errors, are identical. For all three compounds, the c axis coincides with the needle axis of the crystals.

From the density of the zirconium compound, 1.573 ± 0.002 g/ml as determined by flotation methods, the cell content was found to be $3.99 \approx 4$ formula units $\text{Me}(\text{C}_6\text{H}_5\text{N}_2\text{O}_8)_4$.

The following reflections are systematically absent:

$$\begin{aligned} hkl &\text{ with } h + k = \text{odd} \\ h0l &\text{ with } l = \text{odd} \\ 0kl &\text{ with } k = \text{odd} \end{aligned}$$

which is characteristic for the space group No. 60 $Pbcn$.²

The positions of the metal atoms were determined from the three Patterson projections $P(upw)$, $P(pvw)$, and $P(uvp)$ of the zirconium compound (cf. Fig. 1). Their parameters were found to be:

$$\begin{aligned} 4 \text{ Zr in } Pbcn & 4(e): \pm(0, y, \frac{1}{2}); \\ & \pm(\frac{1}{2}, \frac{1}{2} + y, \frac{1}{2}) \text{ with } y = 0.074 \end{aligned}$$

They are thus situated on the twofold axes in the unit cell and consequently have the special extinction: hkl absent for $h+k = \text{odd}$. The fact that the metal ions are situated in this way is also consistent with a "propeller" arrangement since the organic ligands, lacking twofold symmetry, must be situated outside the twofold axes and, consequently, must be paired within the complexes.

The determination of the O, N, and C parameters has also been begun. It was possible to determine the majority of the signs of F_{hko} and F_{0kl} , whereas, because of the special extinctions for the Me atoms, only half of the signs of F_{h0l} could be determined. In this way, reliable electron density maps $\rho(xyz)$ and $\rho(yz)$ could be obtained. The work to interpret these projections and to find out the arrangement of the oxygen, nitrogen, and carbon atoms is continuing.

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Chromatographic Separation of Aliphatic Monocarbonyl Compounds

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In work on the chromatographic separation of the 2,4-dinitrophenylhydrazones of aliphatic methylketones and aldehydes, Meigh's two-phase methanol-heptane system^{1,2} gave promising results. The separation and identification of components in a mixture was, however, impossible owing to the trailing of the spots. Addition of 10 % glacial acetic acid to the moving phase resulted in well concentrated spots. Ligroin (B.D.H., b.r. 90–110° C) and even a technical petrol fraction (Shell, b.r. 80–110° C) were as effective as pure heptane.

Chromatographic method. The paper (Whatman No. 1) is soaked in methanol, the excess methanol allowed to drip off, and the paper dried for 10–15 minutes at 80° C. It should be used within two hours after this procedure. The hydrazones (0.5–30 μg may be used) are then pipetted on to the paper, which is suspended in a dry trough and left to stand overnight. The chamber should be airtight and the cover provided with holes for filling the troughs. The chamber holds two containers, the one with heptane(ligroin)-in-

methanol, the other with methanol-in-heptane(ligroin), for saturating the atmosphere. In these are dipped strips of filter paper to increase the evaporating surface. In the morning the moving phase, 10 % acetic acid in heptane(ligroin), is poured into the trough. Freshly prepared solutions should always be used. It is essential that the temperature is kept equal around the whole chamber to prevent condensation. For reasons that will appear below, the chromatogram can be run for ca. 1.5 h when the mixture contains hydrazones of the lower aldehydes and ketones. A chromatogram with only higher aldehydes and ketones (5–8 C-atoms) can be run for about 4 h. The spots are clearly brought out in UV-light.

With this method, the following R_F -values were obtained:

Formaldehyde	0.19–0.26
Acetaldehyde	0.29–0.37
Heptaldehyde	0.65–0.71
Acetone	0.40–0.52
2-Butanone	0.48–0.55

Quantitative determination of 2-heptanone and heptaldehyde in fat. The aldehyde or ketone is removed from the fat by steam distillation (20 min)^{10–12}. The distillate is collected in a cooled vessel containing 2 ml of a 0.5 % solution of 2,4-dinitrophenylhydrazine in 2 N HCl. The distillate (ca. 100 ml) is allowed to stand at least 1 h at room temperature and then extracted with diethyl ether until the ether is colourless. The extract is then washed with 2 N HCl and distilled water, the ether evaporated *in vacuo*, and the residue dissolved in chloroform and chromatographed. The spots are cut out and the pieces of paper crushed in test tubes containing 5 ml of 30 % ethanol made 0.2 N with NaOH. Samples of this solution are sucked out with a pipette provided with a G 2 glass sinter and measured after exactly 20 min

2-Pentanone	0.53–0.59
2-Hexanone	0.65
2-Heptanone	0.69–0.79
2-Octanone	0.83

It is obvious that identification should be based on comparison with runs of known preparations. Complete separation of formaldehyde, acetaldehyde, acetone, 2-butanone, 2-pentanone, and 2-heptanone was achieved. The spots of the higher homologues, especially, are slightly elongated, and therefore 2-hexanone and 2-octanone are partly overlapped by the nearest members of the series. Identification is possible, but not quantitative separation. This is perhaps the chief drawback of the system, but it can be almost completely overcome with the aid of Matthias' method³. Another weakness is that after ca. 1.5 h a second solvent front is formed and starts to run up the first one. Apparently this is due to diffusion of the methanol into the acetic acid-heptane mixture and the formation of a new equilibrium. The spots now travel close to the second front and are no longer clearly separated.

Among the methods which the authors have tested^{1–3}, this has been the most satisfactory for aldehydes and ketones of higher molecular weight, whereas the system of Tarbell *et al.*², as modified by Buyske *et al.*⁴, is very useful for chromatography of compounds with 5 C-atoms or less. With Matthias' device³, our method gives equally good separation of these compounds.

in a Beckman spectrophotometer, model DU, at 430 m μ .

The recovery of known amounts of hydrazone run on the paper were: 2-heptanone $76.1 \pm 1.17\%$ ($s = 6.5$, 31 samples); heptaldehyde $76.2 \pm 1.43\%$ ($s = 7.1$, 25 samples). When known amounts were mixed in 10 g of lard the recovery was only $35.5 \pm 1.43\%$ in the range 10–200 μ g, whereas from 1 000 μ g it was $33.1 \pm 0.29\%$. Thus the variation was considerably smaller when the amounts were greater, but the recovery was not improved. The chief reason for the low percentage recovery was probably incomplete formation of the hydrazones.

The absorption of extracts from pieces of paper treated in the same manner as the chromatograms and of equal size as the spots was 0.031 ± 0.0017 ($s = 0.009$, 30 samples). Absorption values lower than 0.050 were therefore not concerned, and the lower limit for the determinations is then 1.25 μ g of 2-heptanonehydrazone or heptaldehydehydrazone, corresponding to about 0.5 μ g of pure ketone or aldehyde. Amounts of about 0.5 μ g of hydrazone can, however, be detected in UV-light.

The quantitative method described here cannot be used as such for determination of ketones and aldehydes with lower R_F -values than the two used in this investiga-

tion. Washing of the ether extract with HCl does not remove all the excess dinitrophenylhydrazine, and this forms five spots, of which one travels about as far as 2-hexanone. The method of Pool and Klose¹³ could most probably be used, however, for purification of the ether extract.

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A Low-Resistance Vapour-Phase Chromatograph Column

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In vapour-phase chromatographic separation of high-boiling compounds, as for instance methyl esters of higher fatty acids, it is convenient to apply low pressures as

this enables the use of correspondingly low column temperatures. It is not possible, however, fully to utilize such a pressure reduction in columns of the usual type, as for instance those in which Celite is used as the inert carrier of the static phase, as the pressure drop is very great, about 400 mm mercury pressure in the case of a column length of 1 m. Cropper and Heywood¹ have suggested the substitution of sodium chloride crystals for Celite, enabling a reduction of the pressure drop to 20 mm mercury per metre of column length, and column packing of this type has been used successfully in this laboratory. However, it would be convenient — for several reasons — to be able to reduce the pressure drop further, and since the technique of vapour-phase chromatography offers many points of resemblance to that of fractional distillation, it would be reasonable to assume that packing elements of the types used in low-pressure fractionating columns might also be applied in a vapour-phase chromatograph column. This assumption has been confirmed by experiments with gauze helices of stainless steel, so-called Dixon Gauze Rings, made from fine-mesh steel gauze.

A column packing was prepared with helices of the above-mentioned type, Griffin & George, Ltd., Cat. No. B24-420, dimensions 1/16" × 1/16", the helices being carefully mixed with a solution of Dow Corning High Vacuum Silicone Grease in ethyl acetate. After evaporation of the solvent, the grease was left as a film which covered the gauze meshes, but did not fill out the interior of the helix. The helices were packed into a 2 m column of stainless steel tubing with an inside diameter of 8 mm. At 200°C, 20 mm outlet pressure and a rate of flow of carrier gas of 8 ml N₂ per min a pressure drop from one end of the column to the other of 4.5 mm mercury was measured. For purposes of comparison it may be mentioned that the pressure drop measured across the same column when packed with sodium chloride crystals, but otherwise under identical working conditions, was found to be 52 mm.

For our experiments a mixture of methyl esters of C₈—C₁₈ fatty acids was used, and it was ascertained that the degree of separation obtained by means of the column was practically the same for both types of packing (see Table 1), but that the elution peaks yielded by the steel gauze packing were of a more perfect shape and more symmetrical. The low pressure drop