wasserfreien Salze D-[Cr en_3] $(ClO_4)_3$ und L-[Cr tn_3]Cl_3 überführt [1], die im Vakuumexsikkator getrocknet und aufbewahrt wurden.

2.) Die Messungen der Absorptionsspektren erfolgten bei einer Schichtdicke von 10 cm mit 0.500 M wässrigen Lösungen der Komplexsalze an einem registrierenden Spektralphotometer CARY 11MS-50.

3.) Die Messung der Rotationsdispersion wurde mit Hilfe einer speziellen Messeinrichtung [9] ebenfalls am CARY 11MS-50 durchgeführt. Die Bestimmung des Analysatorwinkels Θ erfolgte mit einer Eichlösung von D-Sucrose (20 g/100 ml), deren spezifische Drehwerte bei 600, 625 und 650 mμ nach Angaben der Literatur [11] berechnet wurden. Die einzelnen Messdaten waren:

[Cr en_3]$(ClO_4)_3$: 0.300 M, $d = 5$ cm; $\Theta = 7.74 \pm 0.03°$, Schichtdicke der D-Sucrose-Lösung 5 cm.

[Cr tn_3]Cl_3: 0.500 M, $d = 5$ cm; $\Theta = 4.95 \pm 0.01°$, Schichtdicke der D-Sucrose-Lösung 1 cm.

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Note on the Crystal Structure of Niobium Dioxide

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The X-ray powder pattern of niobium dioxide was shown by Brauer[1] to contain the lines corresponding to a structure of rutile type and a considerable number of additional weak reflexions. Magnéli and coworkers [2] found that the pattern could be indexed assuming a tetragonal unit cell with $a = \sqrt{2}\ a_r = 13.71$ Å and $c = 2\ c_r = 5.985$ Å, where a_r and c_r represent the parameters of the subcell of rutile type. The unit cell should thus contain 32 formula units of NbO_2 which was confirmed by density measurements.

The present study has comprised a crystal structure determination on the basis of complete Weissenberg data registered with Cu*K* radiation. The single crystals used were obtained from a sample prepared by melting a mixture of niobium metal and pentoxide in an electric are furnace in an argon atmosphere.

The structure determination was performed applying Fourier methods. All the atoms were found to occupy point positions 16(*f*) of the space-group $I4_1/a$ with the following parameter values corresponding to an *R* value of 0.165 for all observed reflexions.

	x	y	z
Nb_I	0.118	0.125	0.483
Nb_{II}	0.133	0.125	0.016
O_I	0.98_6	0.13_0	0.00_1
O_{II}	0.97_1	0.12_5	0.50_1
O_{III}	0.28_0	0.12_6	0.99_3
O_{IV}	0.26_6	0.11_8	0.50_3

The structure is built up of NbO_6 octahedra which are joined by edges and corners as in the rutile structure. However, within the strings of octahedra running in the *c* axis direction, the Nb—Nb distances are alternately shorter (2.80 Å) and longer (3.20 Å). The metal atom pairs thus present in the structure are likely to be associated with the remarkably low value of the magnetic susceptibility observed by Brauer [3]. The Nb—O and O—O distances have throughout normal values, being in the ranges 2.0–2.1 Å and 2.6–3.0 Å, respectively.

Full details on this study will be published elsewhere.

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A High-Field Emission Ionization Detector for Gas Chromatography

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In addition to the various ways, reviewed by Lovelock [1], of providing primary electrons for ionization in gases, high field emission may be used. The detector tube constructed by Haahti and Nikkari [2,3], which obviously depends on field emission, is reported to function only at high temperatures [4]. A field emission-type ionization detector working at normal pressure and temperature with argon as carrier gas is described in this communication.

At normal temperature and pressure the current in commercial argon between electrodes 1 cm apart and at a potential difference of 1 000 V is about 10^{-12} to 10^{-11} A. This current is considerably higher than that between clean electrode surfaces in purified argon. This is explained by the fact that oxide or tarnish films on the electrode surfaces and impurities in the gas may greatly enhance the electron emission due to high fields [5].

If the voltage gradient is sufficiently high, there will be a small concentration of metastable argon atoms in the interelectrode space. At a certain concentration of vapour molecules with an ionization energy ≤ 11.6 eV, the probability of a collision leading to ionization between a vapour molecule and a metastable argon atom will be high. Because the rate of such a double impact ionization process is proportional to the square of the current [5], an electron avalanche will result, where collisions between vapour molecules and metastable argon atoms occur as intermediate stages. With such a mechanism it should be possible to make the ionization current dependent on the concentration of vapour molecules in the electric field [4].

On attempts to use the tube of Haahti and Nikkari at lower temperatures the tube was observed to work according to an "all-or-none" principle; the current impulse started by a minimum vapour concentration was limited by the associated circuit only. Because the too rapid current rise could be due to secondary processes at the cathode (liberation of secondary electrons due to positive ions, photons, or metastables), different geometries and cathode materials were tested.

The experiments were made with commercial argon led into the ionization tube under test through a short chromatographic column. The gas rates varied between 50 and 200 cm^3/min. The temperature was + 18°C. The resistance in series with the ionization tube and the source of highvoltage (800–1 200 V) was $6 \times 10^9 \Omega$. The potential difference across part of the series resistance was fed through a simple impedance converter into a potentiometric recorder.

With aluminium electrodes an increase of the interelectrode distance by ~100 % and/or a decrease of the surface-area of the cathode to ~ 1/20 of the dimensions reported by Haahti and Nikkari [3] led to a response roughly dependent on the concentration of organic vapour in the argon. The tube was observed to have a time lag of some seconds. With the aluminum electrodes a "dead period" was also observed; when the signal had passed, the sensitivity of the tube to the following samples of organic vapour was nil or greatly reduced during a time varying between 30 sec and several minutes. This "dead period" is suggested to be due to a transitory change of the emissive properties of the aluminum surface because of the local heating generated upon impact of positive ions. It is probable that when the tube constructed by Haahti and Nikkari is operated at an elevated temperature not only the concentration of metastables is higher because of the greater acceleration of electrons in the electric field, but also that tarnish films on the electrode surfaces are absent or differ structurally from those on the electrodes at low temperatures.

When the cathode was made of tungsten wire, a higher field was required to obtain the