Four techniques for determining the chromium concentration in ruby are outlined: a chemical, a magnetic, an optical, and a radiospectroscopic technique. The limitations and the applicability of the four techniques are compared. The coefficient for calculating the optical absorption, arising from chromium concentrations determined by magnetic measurements, is 0.29.

In the last few years, synthetic ruby has been widely used in quantum amplifiers and generators of radio frequencies and optical frequencies. In some cases one has to know the concentration $C$ of trivalent $Cr^{3+}$ ions which can isomorphically replace the ions of trivalent aluminum in the crystal lattice of $\alpha-Al_2O_3$. To determine the concentrations, one may employ chemical [1], optical [2-4], and radiospectroscopic techniques as well as a magnetic method [5] which has been developed only recently and is based on the measurement of the anisotropy of the magnetic susceptibility of ruby at the temperature of liquid helium.

This paper compares these techniques* and also gives results of studies made on ruby samples with various chromium concentrations (the figures refer to percent by weight). We note that in the case of ruby, the chromium concentrations $C$ expressed in percent by weight agree to within 2-9% with the $C$ values expressed in mole percent.

**Chemical Analysis.** Small amounts of chromium in ruby were determined using a colorimetric method employing a diphenyl carbazide reaction [9-11]. In acid solution, diphenyl carbazide reacts with hexavalent chromium to form a soluble red-violet complex [12]. The optimum acidity is 0.2 N (sulfuric acid). Then the color develops within several seconds and is stable. Solutions of double-recrystallized potassium dichromate $K_2Cr_2O_7$ were used as standards. In the analysis, a sample of 0.1-0.15 g is crushed in an agate mortar, screened through a Nylon sieve, and melted in a platinum crucible with ten times the amount of a borax/soda mixture (2:3). During the melting, the trivalent chromium transforms almost completely into hexavalent chromium. The melt is leached out with hot water. The solution is then filtered and neutralized with sulfuric acid until an acidity of 0.2 N is obtained. The complete oxidation of the remaining trivalent chromium is achieved by adding ammonium persulfate (1 g of the dry salt) in the presence of a small quantity of $AgNO_3$ as catalyst; afterwards, a diphenyl carbazide solution in 50% acetone is added and colorimetric measurements are made on an FEKN-57 photocolorimeter.

The sensitivity of this method amounts to approximately $10^{-5}$% and is limited only by the purity of the reagents. The accuracy of the method was determined by several independent analyses and amounted to approximately 10% of the chromium quantity determined at chromium concentrations of the order of 0.05%.

The total number of chromium atoms in the sample is determined chemically. This method neither distinguishes between chromium ions which may be isomorphically or nonisomorphically incorporated in the crystal lattice nor between ions of various valence numbers.

**Magnetic method.** The determination of trivalent chromium ions by this method is based on measurements of the temperature dependence of the magnetic anisotropy of ruby at liquid helium temperatures; these measurements are usually made with magnetic torsion balances [5].

The $Cr^{3+}$ concentration is given by the equation

$$N = A \tan \beta,$$

where $N$ is the number of $Cr^{3+}$ ions in the sample, $A = (1.975 \pm 0.005) \cdot 10^{24}$ is a constant which can be expressed by spectroscopic parameters ($g_\perp$, $g_\parallel$, and $D$); $\tan \beta = K T^2 / H^2 \cdot \sin 2\varphi$; $K$ is the absolute value of the torque acting on the ruby sample in a uniform magnetic field, $T$ is the absolute temperature, $H$ is the magnetic field strength, and $\varphi$ is the angle between the optic axis of the crystal and the direction of the magnetic field. With sensitivities of the magnetic balances on the order of $10^{-4}$ dyn·cm, and magnetic field strengths of about 3 kOe, the sensitivity of the $N$ determination

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*The luminescence technique for determining the $Cr^{3+}$ concentration [6-8] is not considered here because in the majority of the samples investigated, the $Cr^{3+}$ concentration was small, whereas the luminescence method becomes sufficiently sensitive only at chromium concentrations of more than 0.2%.
amounts to $10^{14}$ Cr$^{3+}$ ions, i.e., concentrations of $10^{-4}$ to $10^{-5}$% in samples with a weight of approximately 0.1 g.* The accuracy of the method is approximately ± 5%.

Using the magnetic method, the number of Cr$^{3+}$ ions which are isomorphically incorporated in the crystal lattice can be determined. This method is very sensitive and does not require any preliminary treatment of the sample. It is a disadvantage of this method that the measurements must be made at liquid helium temperatures.

**Optical method.** The determination of Cr$^{3+}$, by this method, is based on measurements of the optical density $D = \log_{10}(I_0/I)$ (where $I_0$ and $I$ denote the intensities of the incident and the transmitted light, respectively) for the ordinary wave in the maximum of the broad absorption band of ruby (at 555 nm). It is known [2–4] that the absorption coefficient $\alpha = D/d$ (d denotes the sample thickness in cm) is related to the concentration C by

$$C = \alpha x,$$

where $\alpha$ is a calibration coefficient which can be determined by some absolute method (for example, some chemical or magnetic method). The light losses resulting from reflections from the sample surface and from light scattering in the sample volume are usually determined by measuring $x$ at the wavelength 680 nm, where the intrinsic absorption of the Cr$^{3+}$ ions vanishes. The calculations are made using the equation

$$C = \alpha (x_{680} - x_{880}).$$

In [2–4], the value of the calibration coefficient $\alpha$ was established by a chemical determination of the chromium concentration. The $\alpha$ values obtained there are 0.31 [2], 0.34 [3], and 0.35 [4] for the ordinary ray.**

In our work, the optical density was measured on a nonpolarized light on an SF-4 spectrophotometer. Plane-parallel plates which had been cut perpendicular to the optic axis of the crystal, served as samples. The thickness of these samples was chosen so that the optical density fell in the range 0.3–1.5; then the greatest accuracy of the D determinations is obtained; it amounts to 2–3%. Using the optical method, the chromium concentration in the entire volume of a sample, as well as in individual sample sections, can be determined.

**Radiospectroscopic method.** The chromium-ion concentration in ruby can be measured using the electron-paramagnetic method. At resonance, ruby absorbs the high-frequency power $P$ which can be expressed in the form

$$P = \frac{\pi N \nu}{2kT} \left| M_{ik} \right|^2 \frac{H_1^2}{\hbar} g(\nu),$$

where $N$ is the number of Cr$^{3+}$ ions contributing to the EPR line, $\nu$ is the transition frequency, $T$ is the temperature, $|M_{ik}|$ is the matrix element for the transition between the levels $i$ and $k$, $H_1$ is the strength of the high-frequency magnetic field in the resonator, and $g(\nu)$ is a factor which accounts for the line shape. It is usually very difficult to make an absolute determination of the $P$ value itself and to measure the strength of the high-frequency magnetic field, $H_1$, in the resonator with a sufficient degree of accuracy.

Relative measurements give good results. In this method, a standard sample (e.g., a definite amount of diphenyl picryl hydrazyl, which gives an intense EPR line at room temperature) is placed inside the resonator. In the same resonator, the ruby sample under investigation is placed at a well-defined point; the sample has the form of a standard plate with a thickness of up to one millimeter. The EPR line can be observed on the screen of an oscilloscope whose time base is synchronized with the external field. The sensitivity of such a radiospectroscope is calibrated with the signal from a standard sample; then the area of the absorption curves, which are obtained at a certain line in the EPR spectrum of chromium samples, is measured. The area of the curve can be calculated from the EPR line contour recorded by the recording pen; the scanning of the lines is achieved by changing the amplification of the vertical and horizontal oscilloscope channels. After each sample replacement, the set is recalibrated with the standard signal at fixed oscilloscope amplification.

The number $N$ of chromium ions in the samples 1 and 2 is given by the relation

$$N x x' = N x y' y^' = N y x x' = N y y',$$

Here $k^x$ and $k^y$ are the gain of the oscilloscope for the x and y directions. If the chromium concentration in one of the samples to be measured is known, this sample can be used as the standard and the chromium concentration in the other samples can be determined using Eq. (5).

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* The weight of the samples investigated is indicated in the table.

** In [13], the $\alpha$ values were 0.22 and 0.32 for samples with the concentrations 0.08 and 0.9, respectively. But, as the author of that paper states, his values are not definite, final results.