

Physics. — *On the absorption-spectrum of chromium-oxy-chloride.* By
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The vapour of chromium-oxy-chloride, CrO_2Cl_2 , otherwise chromyl-chloride, absorbs all visible light with wave-lengths smaller than ca. 5000 ÅE. The limit of the range of absorption is very vague and depends greatly on the density of the vapour and on the length of the path, which the light travels. Besides this continuous absorption there is an absorption spectrum which exhibits many lines between ca. 5900 and less than 5000 ÅE. The liquid absorbs continuously all light with wave-lengths smaller than ca. 6000 ÅE.

These facts were already known by STONEY and REYNOLDS, who, according to KAYSER (*Handbuch der Spectroscopie*, III, page 367), observed this spectrum for the first time in 1871. Afterwards only F. KÄBITZ (Diss. Bonn, 1905) effected measurements, which have been communicated by KAYSER (l.c.). The precision of these determinations amounts to some Angström-units. The fact, that KÄBITZ could locate all observed lines in five series, induced us to undertake a closer examination. It is not surprising that there existed a rather constant difference of wavelength between succeeding lines of each of the series, the range of the absorption being small. The difference of the wave-numbers of the lines turned out to have a much more constant value.

In order to enable an accurate measurement of the wave-lengths it proved necessary to make use of low pressures of the vapour. Indeed the lines get fine by lowering the pressure and at the same time the intensity of the continuous absorption diminishes greatly, more than the intensity of the line absorption.

The pressure in the absorption-tube was regulated in the following way. A lateral tube with a not too small quantity of liquid chromyl-chloride was kept at constant temperature in a Dewar-vessel filled with alcohol. The alcohol was cooled by a stream of liquid air, which was siphoned out of a reservoir into a U-tube, placed in the alcohol, where it evaporated and flowed away in gaseous state.

The velocity of flow could be regulated, and thereby the temperature of the alcohol in the stationary state.

This apparatus, provided with a stirrer with a funnel (which was not even necessary for our research) is very suitable for keeping constant temperatures, which are not too low, to within some hundredths of a

degree; this is pointed out by HENNING in *Temperaturmessung*, 1915, page 221.

Many hours at a stretch the temperature (measured with a constantan-iron thermo-element, connected with a potentiometer of Cambridge and Paul's Co) was constant within a range of some tenths of a degree, quite sufficient for our purpose.

The filling of the absorption-tube caused some difficulty, as the chromyl-chloride is impaired or decomposed by all organic compounds and also by mercury and water.

Clouds of HCl are formed with aqueous vapour, preventing the appearance of the fine absorption-lines. The solid CrO_3 which is formed during this reaction, has practically no vapour, so it cannot influence the absorption appreciably.

The chromyl-chloride, produced by KAHLBAUM in small scaled off vessels each containing 2 grams, might also contain HCl. In order to remove this contamination the filling was done in the following way, represented schematically in figure 1.

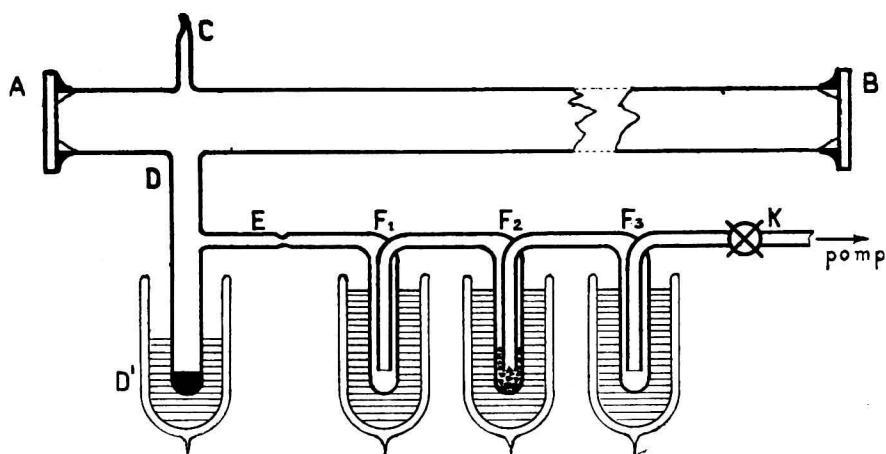


Fig. 1.

The absorption-tube AB had a lateral tube D , above which a small lateral tube C has been blown; by C a small quantity (e.g. 6 grams) of chromyl-chloride was introduced into D ; thereupon C was closed. The bottom of D was then plunged in liquid air and the tube was connected by the tap K with a Langmuir-pump, which evacuated the vessel provisionally.

Between D and K some moisture-traps F_1 , F_2 , F_3 had been blown on, each of which was plunged in liquid air, F_2 containing cocoa nut coal. These traps prevented the vapour of chromyl-chloride from penetrating to K .

Now the pumping was continued with the vessel *D'* containing liquid air, removed. The chromyl-chloride present in *D* melted (at ca. -100° Cent.), filled the tube with vapour and ended by boiling vehemently, in the meantime releasing the dissolved HCl. Thereupon *D* was again cooled with liquid air. This operation was repeated some times, till *D* retained no more than 1 cm^3 chromyl-chloride. The tube *E* was then blown off and the absorption tube was ready for observation.

To get a perceptible selective absorption at very low pressures, it was necessary to make the length of the absorption-tube very large. The best results were obtained with a tube of four metres. A diameter of 5 cm. was necessary to lead the light such a distance through the vapour. The ends had been provided with pieces of plate-glass to prevent loss of light by irregular refraction.

These pieces were too large to be blown in into the tube, so they had to be cemented on its ends. Piceine and other sealing-waxes are impaired strongly by the vapour of chromyl-chloride. Therefore they were cemented with heat-isolation material smeared on the outside with piceine. In this way the vacuum could be kept for several weeks; the piceine was protected sufficiently against the disintegrating influence of the vapour.

When the absorption-tube had been filled for a long time, the walls were covered by a brown layer, which however did not show any absorption-lines in the spectrum, as appeared from some exposures. So no inconvenience in studying absorption of the vapour had to be feared from an eventual covering of the pieces of plateglass by such a brown layer.

The absorption-spectrum was photographed with a Rowland-grating of 14438 lines to the inch (radius of curvature 10 feet) in stigmatic mounting. This mounting has been excellently constructed in the workshop of the laboratory under direction of Mr P. VAN DEN AKKER after the data of MEGGERS and BURNS (Sc. Pap. Bur. of Stand., No. 441, 1922); besides its stigmatism it has the advantage of yielding very luminous spectra, whose dispersion indeed is smaller than in Rowland's mounting, but whose resolving power is not less.

The resolving power of the grating in the first spectrum, which has been always used in this research, is 50000, its dispersion 11 *AE* per mm. The width of the slit was .09 mm during most of the exposures.

At first use was made of a Philips tungsten arc lamp (35 Watts). The times of exposure were however too long with it, at least 28 hours. A small carbon-arc then was used. The surface-brightness of the crater was increased by feeding the lamp with 8 A instead of its normal current of 3 A.

The light was rendered parallel by an achromatic lens, then sent through the absorption tube and sent back through the tube by a mirror at the further end. The light now leaving the tube the second time was

concentrated by a total-reflecting prism and a second achromatic lens on the slit of the spectrograph. The path of the light in the vapour of chromyl-chloride thus amounted to eight metres.

The exposures were made on "Kodak Commercial Panchromatic Films" (5 by 30 cm). The measuring always took place by means of a comparison-spectrum of iron, obtained by changing one of the carbons of the arc for a small iron rod.

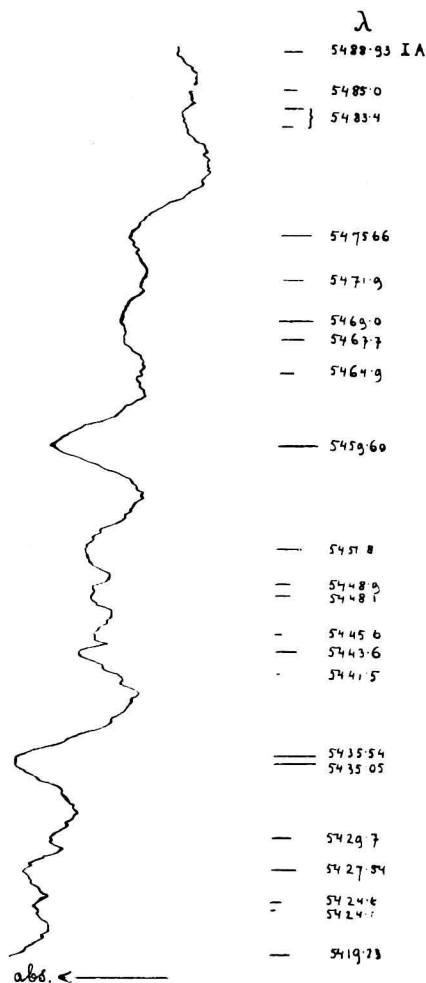


Fig. 2.

Photogram of a part of a negative

11 AE = 1 mm on the negative = 4 cm on the photogram = 19 mm on this reproduction.

The measuring of the negatives obtained was done on a comparator of the Société Gènevoise; the errors of its screw are automatically corrected by an appropriate shift of the zeropoint of the vernier on which the readings are taken. The attainable accuracy is in the neighbourhood of .001 mm. corresponding at the given dispersion with ca. .011 AE.

TABLE.

Int.	λ in I. A.	$1 : \lambda_{vac.}$	Int.	λ in I. A.	$1 : \lambda_{vac.}$
2	5899·25	16946·6	2	5646·5	17705·2
2	5865·45	17044·3	1	5645·9	17707·1
2	5844·73	17104·7	1	5643·3	17715·2
2	5826·2	17159·1	1	5641·5	17720·9
2	5817·00	17186·2	8 } }	5639·28	17727·8
2	5809·2	17209·3		5638·6	17730·0
5	5798·78	17240·2	1	5636·9	17735·3
3	5791·3	17262·5	2	5631·3	17753·0
3	5781·4	17292·1	1	5628·3	17762·4
3	5772·31	17319·3	1	5625·9	17770·0
8	5753·87	17374·8 1)	1	5623·7	17777·0
3	5744·9	17401·9	10 } }	5622·61	17780·4
5	5735·1	17431·7		5622·17	17781·8
5	5726·97	17456·4		5621·52	17783·9
10	5709·26	17510·6 2)	1	5619·2	17791·2
2	5701·1	17535·6	2	5616·8	17798·8
5	5690·4	17569·0	4	5615·50	17802·9
5	5682·86	17591·9	3	5614·35	17806·6
1	5674·7	17617·2	2	5610·6	17818·5
2	5667·3	17640·2	1	5608·0	17826·7
10 } }	5665·77	17645·0	1	5607·40	17828·6
	5665·03	17647·3	1	5606·66	17831·0
1	5663·1	17653·3	1	5606·1	17832·8
1	5661·5	17658·3	3	5605·2	17835·6
3	5658·0	17669·1	3	5604·5	17837·9
3	5657·1	17671·1	3	5603·5	17841·0
1	5653·7	17682·6	1	5602·2	17845·2
2	5650·5	17692·6	2	5599·7	17853·2
1	5648·2	17699·9	1	5598·0	17858·6

1) Double, distance of the components: ·66 AE or 2·0 frequency units.

2) Double, distance of the components: ·84 AE or 2·5 frequency units.

TABLE (Continued).

Int.	λ in I. A.	$1 : \lambda_{vac.}$	Int.	λ in I. A.	$1 : \lambda_{vac.}$	
10	5596·82	17862·3	1	5547·4	18021·5	
	5596·30	17864·0	1	5546·2	18025·4	
	5595·75	17865·8	1	5545·4	18028·0	
1	5594·2	17870·7	1	5544·3	18031·5	
1	5593·2	17873·9	1	5541·9	18039·4	
1	5591·1	17880·6	10	5541·14	18041·8	
1	5590·1	17883·8		1	5539·2	18048·1
1	5589·3	17886·4		15	1	5538·5
1	5588·1	17890·1	0		5537·8	18052·7
1	5586·7	17894·7	2	5537·34	18054·2	
1	5583·8	17904·0	4	5532·7	18069·4	
3	5582·15	17909·3	5	5530·12	18077·8	
3	5580·38	17915·0	3	5524·62	18095·8	
10	5579·9	17916·5	2	5519·6	18112·2	
	5579·1	17919·1	5	5517·3	18119·8	
	5577·5	17924·2		5516·2	18123·4	
1	5574·6	17933·5	10	5512·9	18134·1	
1	5573·5	17937·1		5511·2	18139·8	
3	5572·45	17940·5	3	5509·0	18147·1	
3	5570·90	17945·4	2	5507·2	18153·0	
2	5564·6	17965·8	10	5500·6	18174·8	
4	5561·4	17976·1		5500·05	18176·6	
2	5558·7	17984·8	5	5491·19	18203·6	
2	5557·6	17988·4	5	5488·93	18213·4	
1	5556·1	17993·3	5	5485·0	18226·5	
1	5555·6	17994·9		5483·4	18231·8	
10	5554·92	17997·1	8	5475·66	18257·6	
	5552·93	18003·5	6	5471·9	18270·1	
2	5549·3	18015·8	8	5469·0	18279·8	
1	5548·5	18017·9		5467·7	18284·2	

TABLE (Continued).

Int.	λ in I. A.	1 : λ_{vac} .	Int.	λ in I. A.	1 : λ_{vac} .
3	5464·9	18293·5	4	5347·34	18695·7
10	5459·60	18311·3	10	5341·27	18716·9
5	5451·8	18337·5	8	5333·62	18743·8
4 {	5448·9	18347·2	5	5325·46	18772·5
	5448·1	18349·9	10	5317·93	18799·1
2	5445·6	18358·4	4	5309·18	18830·1
5	5443·6	18365·1	6	5302·51	18853·8
1	5441·5	18372·2	10	5295·07	18880·3
10 {	5435·54	18392·3	3	5284·92	18916·5
	5435·05	18394·0	10	5279·53	18935·8
1	5429·7	18412·1	5	5271·05	18966·3
2	5427·54	18419·3	10	5258·32	19012·7
4	5424·6	18429·4	8	5249·51	19044·1
2	5424·1	18431·1	8	5234·26	19099·6
10	5419·23	18447·7	10	5221·18	19147·4
1	5411·4	18474·4	2	5211·86	19181·7
5	5410·8	18476·4	3	5206·4	19201·8
3	5409·4	18481·2	8	5198·50	19231·0
3	5406·8	18490·1	8	5183·99	19284·8
1	5405·0	18496·3	3	5175·44	19316·7
3 {	5403·5	18501·4	10	5165·43	19354·1
	5402·2	18505·8	2	5161·70	19368·1
10 {	5396·07	18526·9	3	5151·3	19407·2
	5395·03	18530·4	5	5139·4	19452·1
5	5386·83	18558·6	5	5129·4	19490·0
5	5384·4	18567·0	5	5125·0	19506·8
10	5379·84	18582·8	4	5099·7	19603·5
8	5372·48	18608·2	4	5082·5	19669·9
6 {	5364·61	18635·5	5	5056·5	19771·0
	5364·04	18637·5	5	5036·4	19849·9
	5363·56	18639·2	5	5018·3	19921·5
10	5356·68	18663·1			

In the case of the sharp and strong absorption-lines an accuracy in the measurement of the wave-length of 1 : 50000 was within reach, as appears from the following independent determinations.

negative 5,6-I-1926	negative 2,21-IX-1926	difference
5500.07	5500.04	+ .3 : 50000
5459.56	5459.63	— .6 : 50000
5435.27	5435.33	— .5 : 50000
5419.30	5419.16	+ 1.3 : 50000
5379.85	5379.83	+ .2 : 50000

The wave-length was always determined by interpolation between two lines of the iron spectrum, whose wave-lengths were looked up in KAYSER'S Handbuch, VII, 1924.

Each independent measurement of an iron line or an absorption line represents six independent settings. In this way 58 lines of the absorption spectrum were determined in International Angström units.

The first visual observations of the absorption spectrum at low pressures proved already that many of the strong lines are doublets or triplets. The lowering of the pressure revealed the complexity of the lines. At the same time the components themselves also got weaker, so much that it appeared impossible to resolve them completely. We resolved therefore to produce photograms of the negatives by means of a micro-photometer after MOLL. At this instance I was glad to secure the help of Mr ir. W. DE JONG, who placed at my disposal the micro-photometer of the mineralogical laboratory of the Technical High School, made by him. Once more I desire to express my thanks for his kindness. Also to prof. ir. J. A. GRUTTERINK I am much indebted for his kind permission for the use of this instrument.

To distinguish casual peaks in the micro-photogram from real lines several photograms were made from five different negatives, altogether 18 photograms.

On some of these 1 mm. of the negative corresponds with 6 mm. of the photogram; on other ones the magnification was stronger viz. fortyfold.

The measuring of the photograms soon showed the possibility to determine with their aid the wave-lengths of all real peaks, using as standards the lines, whose wave-lengths had been determined directly on the negatives. The feebly and the strongly magnified photograms yielded wave-lengths which agreed well with each other, viz. 2 or 3 : 50000.

Only those peaks were measured (on the comparator) which occurred on photograms of at least three negatives.

The wave-lengths obtained in this way in International Angström units are given in the table. In the first column the estimated intensities are given, in column 2 the wave-lengths determined by direct measurements of the negatives and by the photograms.

Finally the wave-numbers in vacuo are mentioned in the last column. Their calculation was much facilitated by the well known "Tabelle der

Schwingungszahlen" of KAYSER (1925). The numbers printed in heavy type have a precision of 0.4 units, the other ones of 1 unit.

We hope to be able to communicate something before long about the classification of the absorption lines.

Finally I wish to express my thanks to prof. FOKKER for his interest and his valuable support during this research.

Physical Laboratory of the Technical High School.

Delft, Dec. 1926.
