The identity of mottramite and psittacinite with cupriferous descloizite.

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MR. ARTHUR RUSSELL collected in 1930 on Pim Hill, near the village of Harmer Hill, 6 miles north of Shrewsbury, Shropshire, specimens of Triassic sandstone encrusted with minute black crystals. They resemble very closely the material from Mottram St. Andrew, Cheshire, which was described and named mottramite by Sir Henry E. Roscoe in 1876.[1] Mr. Russell pointed out this resemblance and kindly placed his specimens of this rare British mineral at our disposal for investigation. During the course of identifying the incrustations it was found necessary to examine a number of specimens of closely allied minerals—descloizite, cuprodescloizite, psittacinite, &c. X-ray powder photography and chemical analysis were the methods used, and approximate optical data were obtained whenever possible. The specimens studied included as far as possible material from type localities, and are listed below :

I. Large black pyramidal crystals, labelled descloizite, yielding a pale-yellow powder; from Abenab, South-West Africa, collected by Dr. L. J. Spencer, 1929. (B.M. 1929,1946a.)

II. Large dark-brown pyramidal crystals with curved faces, labelled descloizite, yielding an olive-green powder; from Grootfontein district, South-West Africa. (B.M. 1930,296.)

III. Grass-green crystals, labelled cuprodescloizite, yielding a bright-green powder; from Uris mine, Tsumeb, South-West Africa. (B.M. 1931,22.)

IV. Olive-green botryoidal, fibrous mass, labelled mottramite, yielding an olive-green powder; from Nageib, Otavi district, South-West Africa. (B.M. 1929,1871.)

V. Thin incrustations of minute black crystals, yielding an olive-green powder; on sandstone from Pim Hill, Harmer Hill, Shrewsbury, Shropshire, collected by Mr. Arthur Russell, 1930.

[1] H. E. Roscoe, Proc. Roy. Soc. London, 1876, vol. 25, p. 111.

VI. Red, compact mamillary crusts, with A. Krantz's label ' dechenite ', yielding an orange-yellow powder; from Niederschlettenbach, Lauterthal, Rhenish Bavaria. (B.M. 26521.) C. Bergemann [1] gave this name to a mineral collected by A. Krantz, and his chemical analyses suggested it to be a simple lead vanadate. Although G. J. Brush [2] and F. Pisani [3] detected the presence of zinc in material from the same locality, no quantitative chemical work on the mineral has been carried out since 1854. A. Krantz considered that araeoxene [4] from Dahn, Lauterthal, Rhenish Bavaria, is identical with dechenite. The two localities are only a mile apart, and Bergemann's [5] analysis of material from Dahn shows 10·52 % As_2O_5.

The following specimens were examined only by X-ray powder photographs and optical methods, owing to insufficient material for chemical analysis:

VII. Siskin-green compact material from Iron Rod mine, Silver Star district, Montana, U.S.A. (B.M. 63521.) F. A. Genth [6] received in 1874 similar material from the same locality, which he erroneously described as a new tellurate of lead and copper. He did not analyse the mineral until 1876,[7] and then found it to be a copper lead vanadate which he named ' " psittacinite " from psittacinus, siskin- or rather parrot-green '.

VIII. Thin black incrustations yielding an olive-green powder; on sandstone from Mottram St. Andrew, Cheshire. (B.M. 52314.) This specimen of the original mottramite was presented to the British Museum by Sir Henry Roscoe in 1879.

IX. Black crusts of iridescent crystals, labelled psittacinite, yielding an olive-green powder; from Shattuck-Arizona mine, Bisbee, Arizona, U.S.A. (B.M. 1913,383). This material is probably identical with that described by Wells [8] as cuprodescloizite and later renamed psittacinite by Schaller.[9]

X. Dark-green incrustations, yielding an olive-green powder, labelled vanadinite on sandstone; from near Shrewsbury, Shropshire, bequeathed by Miss Caroline Birley. (B.M. 1907,912.) This material no doubt came from the same locality as Mr. Russell's specimens.

XI. Thin black, botryoidal, iridescent crust, yielding a yellow powder, on massive cerussite and pyromorphite with galena, &c.; from Leadhills, Lanarkshire. (B.M. 51280.) This specimen was presented and described by T. Davies [10] as vauquelinite. Mr. W. Campbell Smith in 1922 detected the presence of vanadium and water, and Mr. Hey in 1929 detected lead, copper, and vanadium, but no chromium or zinc.

XII. Thin black crust, yielding a canary-yellow powder, with vanadinite on massive pyromorphite, from Wanlockhead, Dumfriesshire. (B.M. 51281.) This

[1] C. Bergemann, Ann. Phys. Chem. (Poggendorff), 1850, vol. 80, p. 393.

[2] G. J. Brush, Amer. Journ. Sci., 1857, ser. 2, vol. 24, p. 116.

[3] F. Pisani, Bull. Soc. Franç. Min., 1889, vol. 12, p. 40.

[4] F. von Kobell, Journ. Prakt. Chem. (Erdmann), 1850, vol. 50, p. 496.

[5] C. Bergemann, Neues Jahrb. Min., 1857, p. 397.

[6] F. A. Genth, Proc. Amer. Phil. Soc., 1876, vol. 14 (for 1874–75), p. 229.

[7] F. A. Genth, Amer. Journ. Sci., 1876, ser. 3, vol. 12, p. 35.

[8] R. C. Wells, Amer. Journ. Sci., 1913, ser. 4, vol. 36, p. 636.

[9] S. Taber and W. T. Schaller, Amer. Min., 1930, vol. 15, p. 578. [M.A. 5–46.]

[10] T. Davies, Min. Mag., 1877, vol. 1, p. 112.

specimen was also presented by T. Davies, who labelled it vauquelinite. Mr. W. Campbell Smith in 1922 labelled the black mineral psittacinite, and Mr. Hey in 1929 detected lead, copper, and vanadium, but no chromium or phosphate. Frenzel[1] analysed the small brown spherules of 'vanadinite' on similar specimens from the same locality and concluded they were descloizite.

XIII. Yellow, powdery substance, coated brown on a heavy, brown, compact matrix; labelled chileite, from Mina Grande, near Arqueros, Chile. (B.M. 39332.) This material is probably the same as that described and analysed by I. Domeyko[2] in 1848.

XIV. Yellow, compact, botryoidal crusts, being one of the original specimens of eusynchite described by H. Fischer and Nessler in 1854,[3] from Hofsgrund, near Freiburg, Baden. (BM. 26942.) Their analyses showed it to be a lead vanadate, but a zinc content was discovered by subsequent workers, and I. Lang[4] carried out analyses and concluded that eusynchite is identical with descloizite.

XV. Deep brown-red descloizite crystals, with calcite and pyrolusite, from Sierra Grande mine, Lake Valley, Sierra Co., New Mexico. (B.M. 56878.) They are similar to crystals from the same locality described and analysed by F. A. Genth.[5] This is the only specimen listed here which yields crystals sufficiently small and perfect to be oriented by goniometric methods for X-ray photographs.

X-ray photographs of powdered material from each of the above specimens are identical (with the possible exception of chileite, no. XIII, which is probably mixed with impurities), and measurements show that there is no appreciable variation in unit-cell dimensions from one specimen to another. With the exception of specimens of compact material it is found that grinding the powdered crystals for a long time fails to reduce the grain sufficiently for powder photographs. In order to obtain an X-ray powder photograph quite free from flecks it is necessary to rotate the powder. Providing the specimen is very carefully centred in the X-ray beam no diminution in sharpness of the lines on the photograph results, and comparison of intensities is then possible.

Rotation, oscillation, and Laue photographs were also taken of a single crystal of descloizite specimen XV. The crystal used for these photographs shows the forms $m(110)$ and $o(111)$ [Dana's axes]. Goniometric measurements yield the axial ratios $a : b : c = 0.645 : 1 : 0.808$, in good agreement with vom Rath's values $(0.6368 : 1 : 0.8045)$ for descloizite from the same locality and with A. Diefenbach's[6] values $(0.6448 : 1 : 0.8022)$ for descloizite from South-West

[1] A. Frenzel, Neues Jahrb. Min., 1875, p. 673.
[2] I. Domeyko, Annales des Mines, Paris, 1848, ser. 4, vol. 14, p. 145.
[3] H. Fischer and Nessler, Ber. Verh. nat. Gesell. Freiburg, 1854, vol. 1, p. 33.
[4] I. Lang, Mitt. Badischen Geol. Landesanstalt, Heidelberg, 1903, vol. 4, p. 510.
[5] F. A. Genth and G. vom Rath, Zeits. Kryst. Min., 1885, vol. 10, p. 464.
[6] A. Diefenbach, Zeits. Krist., 1930, vol. 74, p. 178. [M.A. 4–382.]

Africa. Rotation photographs show that the edge of the ortho-rhombic unit cell are a 6·05, b 9·39, c 7·56 ± 0·03 Å. These values yield the axial ratios 0·644 : 1 : 0·805. Knowing the unit-cell dimensions it was possible to index correctly the powder photographs of I to XIV. Moreover, the diameters of the diffraction rings agree well with those calculated from the spacings for the single crystal. So far, then, identical X-ray photographs have been obtained not only for descloizites from different localities, but also for other minerals of the descloizite group. Table I gives the measurements of an X-ray powder photograph of no. IV.

TABLE I. Measurements of an X-ray powder photograph of specimen IV, mottramite from Nageib, South-West Africa.

| Diameter of rings, cm. | | Index. | In-tensity. | Diameter of rings, cm. | | Index. | In-tensity. |
Observed.	Calculated.			Observed.	Calculated.		
1·85	1·87	(110)	m	3·50	3·503	(211)	m
2·00	1·99	(020)	w	3·57	3·56	(122)	m
2·20	2·215	(111)	w	3·65	3·62	(131)	ms
2·38	2·345	(021)	w	3·73	3·71	(220)	w
2·64	2·675	(012)	w	3·85	3·89	(013)	vw
2·90	2·93	(102)	s	3·93	3·925	(221)	vw
3·11	3·105	(200)	vw	4·12	4·14	(212)	s
3·30	3·255	(031)	m	4·56	4·55	(231)	ms

Diameter of cylindrical camera = 6·04 cm. Cu—K_α radiation with nickel filter was used, λ = 1·539 Å. The calculated diameters of the diffraction rings are based on the unit-cell dimensions found for the single crystal of descloizite (no. XV) a 6·05, b 9·39, c 7·56 ± 0·03 Å. s = strong, m = medium, w = weak, vw = very weak.

Thin sections of crystals from specimens I, II, and III were prepared to see whether any marked zoning is present. Zoning is most marked in specimens I and III, but could not be detected in II. Green crystals from III form distorted, branched, and parallel growths, and only the interior is brown and translucent. The exterior is quite compact, and at first suggested that the green coating might be pseudomorphous. The X-ray and chemical work disprove this, however, and it is more probable that the difference in colour and texture is due to a physical change. Three sections were cut from crystals of specimen I parallel to the faces a(100), and b(010), and c(001) respectively. The section showing the greatest zoning is that parallel to c(001) and perpendicular to the acute bisectrix, the optic axial plane being parallel to b(010). No reliable value of 2E could be obtained, however, since 2V is near 90°. Birefringence measurements

were also rendered difficult because of the deep colour of the mineral and the high birefringence. Approximate refractive index measurements were carried out using fragments of various specimens in sulphur-selenium melts. The mean refractive indices of mottramite and descloizite do not differ by more than 0·05; $n_\alpha = 2·21$, $n_\gamma = 2·33 \pm 0·02$. The birefringences measured by Mr. Hey on the three sections of specimen I are $\gamma - a = 0·12 \pm 0·04$ on $b(010)$, $0·07 \pm 0·02$ on $a(100)$, and $0·06 \pm 0·02$ on $c(001)$. These measurements do not permit a decision as to which is $\beta - a$ and which is $\gamma - \beta$. Sections of specimens II and III not cut in any known direction give values near 0·12. All the sections are highly pleochroic: for specimen I, γ brown-yellow, a and β canary-yellow; and for specimen III, γ brown-yellow, a and β green-yellow.

Table II gives the results of Mr. Hey's chemical analyses of specimens I to VI, together with density determinations. It is difficult

TABLE II. Chemical analyses of descloizite and mottramite.
Specimens I–VI. (By M. H. Hey.)

	I.	II.	III.	IV.	V.	VI.
V_2O_5	22·76	22·73	22·73	22·65	17·66	16·26
As_2O_5	nil	nil	nil	nil	nil	7·13
PbO	55·47	55·78	54·56	54·50	44·50	54·10
CuO	0·56	10·29	16·84	13·90	15·70	0·61
ZnO	19·21	8·86	2·62	5·12	0·57	19·46
FeO*	trace	0·72	0·58	0·53	1·95	trace
MnO	trace	0·01	trace	trace	trace	trace
$H_2O + 350°$ C.... ...	2·17	2·24	2·29	2·09	1·80	2·29
$H_2O - 350°$ C.... ...	0·02	0·12	0·40	0·58	1·08	0·08
SiO_2	0·02	0·11	nil	0·89	16·31	0·27
Total	100·21	100·86	100·02	100·26	99·57	100·20
Oxygen %	17·84	17·82	18·01	18·01	17·75	17·43
Density (obs.) ...	6·26	6·18	5·80	5·96	5·5†	6·24
Density (calc.) ...	6·20	6·21	6·14	6·14	6·23	6·35

NiO, CoO, and P_2O_5 were tested for in nos. I, II, III, IV, and VI and found absent. Weights of material used for analyses V and VI about 0·6 gram; for the other analyses larger amounts were available.

* Total Fe estimated as FeO. In analysis V a part of or perhaps all the iron is present as Fe_2O_3 in the sandstone.

† Corrected for admixed sandstone, but still $\pm 0·5$.

to obtain satisfactory densities of many of these specimens, either because of insufficient material or the fibrous structure of the botryoidal specimens. For this reason densities calculated from the X-ray data are tabulated rather than the number of oxygen atoms per

unit cell. The most reliable density figure was obtained for no. II, the material of which is uniform and free from zoning. Using this figure, the unit-cell dimensions, and the oxygen percentage given by chemical analysis, the number of oxygen atoms per unit cell is calculated to be 17·94 excluding the water content.

The number of vanadium, lead, copper, zinc, &c., atoms per unit cell have been calculated assuming 18 oxygen atoms per unit cell, excluding the water content, for all six analyses. It can be seen from table III that both the lead and vanadium contents are constant at

TABLE III. Number of atoms per unit cell.
(Calculated from Table II.)

			I.	II.	III.	IV.	V.	VI.
V ...	...	...	4·03	4·01	4·01	4·03	3·81	3·97†
Pb ...	...	...	4·00	4·01	3·92	3·95	3·92	4·00
Cu ...	...	...	0·11	2·07	3·40	2·83	3·88	0·13
Zn ...	...	...	3·80	1·75	0·52	1·02	0·14	3·94
Fe ...	...	...	trace	0·16	0·13	0·12	0·53	trace
Mn ...	...	...	trace	0·02	trace	trace	trace	trace
ΣZn*	...	...	3·91	3·98	4·05	3·97	4·55	4·07
H_2O+	...	...	1·94	2·00	2·03	1·87	1·96	2·09
H_2O-	...	...	0·02	0·11	0·36	0·52	1·19	0·07

* ΣZn = Zn+Cu+Mn+Fe.
† Including 1·02 atoms As.

four atoms per unit cell, while the sum of the zinc, copper, iron, and manganese atoms also amounts to four. All previous analyses of the descloizite minerals have been recalculated in the same way to give the number of atoms of each sort in the unit cell. For all analyses in which an accurate separation of zinc from vanadium has been effected the atomic contents show the same relations as Mr. Hey's analyses. Phosphorus and arsenic can replace vanadium up to 0·4 and 1·0 atoms per unit cell respectively, the highest phosphorus and arsenic contents being usually found in botryoidal fibrous forms rather than in well-crystallized specimens. The content of manganese and iron rarely exceeds 0·2 atoms per cell. All the available analyses show that the zinc and copper content can have values ranging from 0 to 4, providing the sum Zn+Cu+Fe+Mn = 4. This suggests a complete isomorphous series between the zinc-rich and the copper-rich descloizites. Taber and Schaller (loc. cit.) have questioned the isomorphism of these two end-members, pointing out that copper-rich descloizite has a higher water content corresponding approximately to twice that found for copper-poor descloizite. Both

Pufahl[1] and Diefenbach[2] have obtained the same results, though they attribute the extra molecule of water to adsorption, and do not consider it to be water of constitution.   This appears to be the correct conclusion for many reasons.

W. F. Hillebrand[3] determined the water content of a dull-yellow friable specimen of compact descloizite from Mayflower mine, Beaverhead Co., Montana, containing only 1·15 % CuO, i.e. 0·25 atoms of Cu per unit cell.   He found for material dried at 100° C. that the water lost on heating to a dull red-heat was 4·37 %, which, recalculated, is equivalent to 4·12 H_2O per unit cell.   I. Lang[4] also found 3 % of H_2O in a specimen of eusynchite from the type locality, but did not record any copper content. These specimens differ from ordinary descloizite in being either fibrous as in eusynchite or compact. Such finely crystalline or powdery material is more often rich in copper; the excess water content is not a direct consequence of high copper content, but is connected with the state of subdivision of the specimen and its previous history.

Although most analysts have recorded the fact that descloizites give up their water content only on heating to a red-heat no data are recorded giving the loss of water at various temperatures. Mr. Hey, employing the method of Dittler and Hueber, determined the amount of water lost at 110°, 200°, 350° C., and a dull red-heat for specimens II, III, IV, and V. He also confirmed the total water contents given in table II by the Penfield method.   The results are shown in table IV.

TABLE IV.   Dehydration data for descloizite and mottramite.
(By M. H. Hey.)

Total loss at:			Loss of water (%).			
			II.	III.	IV.	V.
110° C. ...	...	...	nil	0·09	0·39	0·38
200° C. ...	...	...	nil	0·26	0·39	0·62
350° C. ...	...	...	0·12	0·40	0·58	1·08
Red-heat	...	...	2·36	2·69	2·67	2·88

Total loss at:			Loss of water (molecules).			
			II.	III.	IV.	V.
110° C. ...	...	...	nil	0·08	0·35	0·41
200° C. ...	...	...	nil	0·24	0·35	0·68
350° C. ...	...	...	0·11	0·36	0·52	1·19
Red-heat	...	...	2·11	2·39	2·39	3·17

[1] O. Pufahl, Centralblatt Min., 1920, p. 289. [M.A. 1–150.]
[2] A. Diefenbach, loc. cit., p. 155. [M.A. 4–382.]
[3] W. F. Hillebrand, Bull. U.S. Geol. Survey, 1890, no. 60, p. 130.
[4] I. Lang, Mitt. Badischen Geol. Landesanstalt, Heidelberg, 1903, vol. 4, p. 504.

It is evident from the data in table IV that the water of constitution, present as hydroxyl groups in the crystal-structure, is constant at $2H_2O$ per unit cell. The figure for the water given off below $350°$ C. does not approach any round number and it is greater for those specimens which are cryptocrystalline, viz. III, IV, and V. We hoped that one of the six specimens analysed would show a total figure for the loss of water approaching those found by Diefenbach for mottramite from South-West Africa and those given by Taber and Schaller for so-called psittacinite from Bisbee, Arizona.

Table V shows the total water content shown in recent analyses of mottramite from various localities. The suggestion that variable amounts of water may be absorbed and held up to temperatures of $350°$ C. is the most reasonable explanation of the facts.

TABLE V. Total water content of mottramite from recent analyses.

Locality.	H_2O %.	No. of H_2O mols. per unit cell.	Cu %.	Density.	Analyst.
S.-W. Africa	4·79	4·15	22·08	6·033	Diefenbach, 1930
,, ...	4·38	3·88	20·76	6·107	,,
,, ...	4·31	3·82	19·89	6·121	,,
,, ...	3·92	3·63	19·50	5·900	Pufahl, 1920
,, ...	3·93	3·61	18·75	5·930	,,
Bolivia ...	2·71	2·49	17·72	6·416	Dittler and Hueber, 1931 [1]
Arizona ...	4·79	4·58	19·10	—	Taber and Schaller, 1930
,, ...	3·63	3·39	17·04	—	Wells, 1913 [2]
S.-W. Africa	2·69	2·39	16·84	5·800	Hey, III
,, ...	2·67	2·39	13·90	5·960	,, IV
Harmer Hill	2·88	3·15	15·70	5·5	,, V

It is also important to note that powder photographs of specimens III and IV after being heated for many hours at $350°$ C. are identical with photographs taken before dehydration. It is only the water which is given off at a red-heat that is actually in combination. One further piece of evidence is offered by the X-ray work, and for that reason the description of the space-group determination has been delayed till now.

Oscillation photographs of the single crystal already used for rotation photographs were taken about the b and c axes and when these

[1] E. Dittler and H. Hueber, Min. Petr. Mitt. (Tschermak), 1931, vol. 41, p. 173. [M.A. 4–525.]

[2] R. C. Wells, Amer. Journ. Sci., 1913, ser. 4, vol. 36, p. 637.

were indexed, reflections of the type $(hk0)$ for $(h+k)$ odd and $(h0l)$ for l odd were found to be absent. The space-group is therefore V_h^{16}, which permits only fourfold and eightfold positions in the structure of descloizite. Thus the total number of oxygen atoms per unit cell should be a multiple of four or eight. The work already described shows that this number is approximately twenty. The unit cell would contain 22 oxygen atoms if an extra two molecules of water were included. This possibility is therefore prohibited for descloizite by the space-group determination.

Unfortunately, it has not been possible to isolate a single crystal of mottramite and perform a space-group determination. It may be said, however, that the evidence of the X-ray powder photographs and the chemical work make it almost certain that the water content of mottramite is the same as that of descloizite, and that the higher figures shown by some analyses are due to the cryptocrystalline state of the specimens examined.

The contents of the unit cell of any member of the descloizite group may now be written down from table III as $4PbO.4(Zn,Cu)O.2V_2O_5.2H_2O$; this is equivalent to $4Pb(Zn,Cu)(OH)(VO_4)$. It is probable that the (VO_4) and (OH) units each occupy a fourfold position in the crystal-structure. The constancy of the lead content in descloizite analyses suggests that the lead atoms also occupy a fourfold position, the zinc and copper atoms occupying yet another. The general constitutional formula for descloizite may therefore be written $Pb(Zn,Cu,Mn,Fe)(OH)[(V,As,P)O_4]$.

In the light of X-ray and chemical work there appears to be no case for retaining the three mineral names cuprodescloizite, mottramite, and psittacinite as separate species. It is, however, usual to retain a name for each end of an isomorphous series. The decision in this case rests upon priority. Both mottramite and psittacinite were named in 1876 (see p. 377), actually the latter a month later than mottramite. Cuprodescloizite was the name given by Rammelsberg[1] in 1883 to a mineral containing 8 % CuO and is therefore unsuitable. The only other rival is chileite, which was named by Kenngott[2] in 1853 on the evidence of Domeyko's analyses (1848). Since the name had already been employed by Breithaupt in 1840 for a mineral from Chile, afterwards found to be goethite, and

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[1] C. Rammelsberg, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1883, part 2, p. 1215.

[2] A. Kenngott, Mohs'sche Mineralsystem, Wien, 1853, p. 28.

Domeyko's analyses show an appreciable arsenic content, it would be confusing to retain this name for the copper-rich members of the descloizite group. Mottramite is the most suitable choice on all grounds. The use of the name psittacinite should be discontinued. Descloizite, of course, should be retained for the zinc end of the series. Since there is a complete isomorphous series between descloizite and mottramite, the latter name should be used for those members carrying more than 2 atoms of copper per unit cell, i.e. more than 10 % CuO. From Mr. Hey's analyses, III, IV, and V are therefore mottramites, I and VI descloizites, and II on the border-line. Of the remaining specimens identified by X-ray methods alone previous analyses of similar material show that all are mottramites except nos. XIV and XV.

Summary.—Oscillation, Laue, and rotation photographs show that descloizite has an orthorhombic unit cell with edges a 6·05, b 9·39, c 7·56 Å., and space group V_h^{16}. The unit cell contains $4PbZn(OH)(VO_4)$. Powder photographs of descloizite, cuprodescloizite, mottramite, psittacinite, chileite, eusynchite, and dechenite, from the type localities are identical with each other. New chemical analyses and determinations of the water content at various temperatures, together with the X-ray work, show that all these minerals may be represented by the general formula $Pb(Cu,Zn)(OH)(VO_4)$. Thin incrustations of minute black crystals on sandstone from Harmer Hill, near Shrewsbury, are identical with the original mottramite from Mottram St. Andrew, Cheshire. Mottramite is retained as the most suitable name for all descloizites containing more than 10 % CuO.

Note on the chemical analyses. (By M. H. Hey.)

Since the vanadates present unusual problems in the attainment of accurate analyses, some description of the methods used appears desirable. The method used for the water determination also calls for some comment.

The principal difficulties encountered in vanadate analyses are the tendency of the basic sulphides of group II (especially CuS and PbS) to carry down the corresponding sulphovanadates in appreciable amount, and the tendency of the ammonia precipitate to carry down vanadium by adsorption.[1] A survey of earlier analyses suggests that the first of these sources of error has often been neglected. The difficulty of obtaining complete precipitation of vanadium is best overcome by the use of volumetric methods.

[1] See for example W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analyses, New York, 1929, pp. 352–363. The present method as a whole is, so far as I am aware, new, but is based on the statements and suggestions made in Dr. Hillebrand's admirable account.

The partial precipitation of vanadium in group II was avoided by addition of tartaric acid in amount sufficient to prevent ammonia producing any precipitate. The precipitate so obtained might contain CuS, PbS, As_2S_5, and some ZnS; it was dissolved and the lead removed as sulphate, then copper and zinc precipitated with H_2S in ammoniacal solution and the filtrate examined for arsenic. The copper and zinc sulphides were dissolved, the copper precipitated as cuprous thiocyanate, and the zinc solution reserved.

The filtrate from group II was made ammoniacal and treated with H_2S, precipitating Fe, Zn, Mn, and any Ni and Co, as sulphides. These metals were thus obtained free from tartaric acid, vanadium, and phosphorus, and were separated in the usual way.

Preliminary tests had shown that Ca and Mg were absent, and the alkalis were neglected. The filtrate from the ammonium sulphide group, therefore, had only to be examined for vanadium and phosphorus. It was evaporated down, and the tartaric acid destroyed with sulphuric and nitric acids, and finally $KMnO_4$ added in slight excess; the solution was then reduced with SO_2 and the vanadium estimated volumetrically. For each analysis the solution was reduced and titrated twice; then the vanadium was reduced again and phosphorus tested for with ammonium molybdate. The results of this procedure were highly satisfactory.

FIG. 1. Wash-bottle for determination of water content by Dittler and Hueber's method. (Half actual size.)
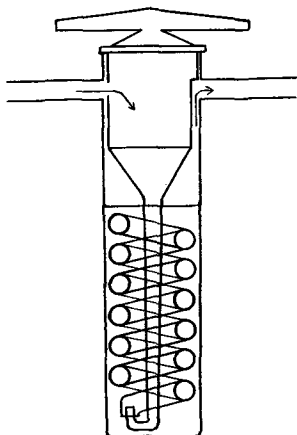
For the estimation of the water, the method of J. Lindner, as modified by E. Dittler and H. Hueber,[1] was employed, and found satisfactory. The only modification made in Dittler and Hueber's apparatus was that the special wash-bottle illustrated by them was replaced by a simpler model, the flat glass spiral, ground in, being replaced by a spiral glass tube. It is somewhat similar to the well-known Walter's pattern, but more compact, and is shut off from the atmosphere by turning the stopper (fig. 1). This pattern of wash-bottle was used both for the α-naphthyl phosphoric chloride and for the alkali. With a bubble rate of 2–3 per second it gives complete reaction or absorption with a single passage.

The somewhat inaccessible reagent employed by Lindner and by Dittler and Hueber, α-naphthyl dichlorphosphine oxide, $C_{10}H_7.POCl_2$, was replaced by α-naphthyl phosphoric chloride, $C_{10}H_7O.POCl_2$, which is readily prepared from α-naphthol and phosphorus oxychloride,[2] and which was found to fulfil the requirements of non-volatility, stability, and quantitative reaction with water perfectly. Preliminary tests showed it to be a quite satisfactory substitute.

[1] E. Dittler and H. Hueber, Zeits. Anorg. Chem., 1930, vol. 195, p. 41; 1931, vol. 199, p. 17. [M.A. 5–141.]

[2] See P. Kunz, Ber. Deut. Chem. Gesell., 1894, vol. 27, part 2, p. 2561.