OCCURRENCE OF BROMINE IN CARNALLITE AND SYLVITE FROM UTAH AND NEW MEXICO*

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Abstract

Both carnallite and sylvite from Eddy County, New Mexico, contain 0.1 per cent of bromine. The bromine content of these minerals from Grand County, Utah, is three times as great. No bromine was detected in halite, polyhalite, långbeinite, or anhydrite from New Mexico. Iodine was not detected in any of these minerals.

On the basis of the bromine content of the sylvite from New Mexico, it is calculated that 7,000 tons of bromine were present in potash salts mined from the Permian basin during the period 1931 to 1945.

Introduction

The Geological Survey has previously made tests for bromine and iodine in core samples of potash salts from New Mexico.[1] Bromine was found to be present in very small amounts. No systematic quantitative determinations were made, nor was the presence of bromine specifically correlated with quantitative mineral composition. Sections of potash core from four recently drilled wells and selected pure saline minerals from Eddy County, New Mexico, together with two cores from Grand County, Utah, were therefore analyzed for their bromine and iodine content. The percentage mineral composition was then correlated with the bromine content. It was found that bromine was restricted to carnallite and sylvite. Iodine was not detected in any of the samples analyzed. If present, its quantity must be less than .005%.

Brine and sea water are the present commercial sources of bromine in the United States, though both Germany and U.S.S.R. have utilized potash salts as a source of bromine.

German potash salts are reported to contain bromine in the following amounts:[2]

Mineral	*Formula*	*% Bromine*
Bischofite	$MgCl_2 \cdot 6H_2O$	0.467
Tachhydrite	$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$	0.438
Carnallite	$MgCl_2 \cdot KCl \cdot 6H_2O$	0.143–0.456
Sylvite	KCl	0.117–0.300
Sylvinite	$KCl+NaCl$	0.085–0.331
Hartsalz	$KCl+NaCl+MgSO_4 \cdot H_2O$	0.027
Långbeinite	$2MgSO_4 \cdot K_2SO_4$	0.016

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[1] Schaller, W. T., and Henderson, E. P., Mineralogy of drill cores from the potash field of New Mexico and Texas: U. S. Dept. Interior. *Geol. Survey, Bull.* **833,** 23 (1932).

[2] Winkler, L. W., The bromine content of German potash salts, original liquors, and end liquors: *Zeit. Angew. Chem.*, **30,** 95–96 (1917) cf. *Chem. Abstracts*, **11,** 2719 (1917).

The first two minerals have not yet been found in any of the potash salts in the United States.

According to Chirkov,[3] bromine and iodine are present in sylvinite from Solikamsk, U.S.S.R., as tabulated below:

Sample	KCl *in sylvinite*	Br *in sylvite*	I *in sylvite*	Br *in halite*	I *in halite*
Sylvite, white	100	0.203	0.0080	—	—
Sylvinite	56.1	0.150	0.0060	0.024	0.0007
Sylvinite	40.1	0.142	0.0055	0.020	0.0009
Halite	0	—	—	0.016	0.0015

Bromine in carnallite from Solikamsk decreases with depth in the bed, from 0.25% at 179.2 meters to 0.07% at the bottom of the bed. Most of the bromine analyses show 0.15 to 0.20% bromine at depths between 200 and 250 feet.[4] A previous article reported the bromine content of Solikamsk carnallites to vary between 0.17 and 0.30%.[5]

The analyzed samples from Utah came from the McCarthy, No. 1 well (McC in Table 1) of the Utah Magnesium Corporation, drilled in the NW ¼ of the NE ¼ sec. 16, T. 22 S., R. 19 E., and from the Wright No. 1 well (W in Table 1) in the SW ¼ of the SW ¼ sec. 4, T. 22 S., R. 19 E.

The analyzed samples from New Mexico were from wells drilled by the Bureau of Mines in T. 20 S., R. 29 E., Eddy County, New Mexico. B M well no. 8 was drilled in section 25, no. 14, in section 26, no. 15 in section 26, and no. 16 in section 14.

The mineralogy of the Utah cores is simple. Halite is the most abundant mineral. It is colorless or gray, medium-grained, and with interlocking grains. Carnallite is also very abundant. Various portions of the core are almost entirely made up of a pale salmon-colored, medium-grained carnallite; less commonly carnallite is colorless or red. Sylvite, which is also abundant in these cores, is usually white, though some fine-grained areas contain red sylvite. The white sylvite occurs as large crystals an inch or more in size, or intergrown with halite in medium-sized grains. Kieserite, anhydrite, and clay were present in small quantities.

The cores from New Mexico contained predominantly colorless halite, brick-red sylvite, and blood-red carnallite, with lesser amounts of pink polyhalite, white kieserite, anhydrite, and red or gray clay.

[3] Chirkov, S. K., Solid solutions of potassium, sodium, and magnesium halides: *Jour. Gen. Chem.* (U.S.S.R.), **14,** 415 (1944).

[4] Chirkov, S. K., *lit. cit.*, p. 417.

[5] Efreman, N. N., and Veselovskii, A. A., Bromine contents of Solikamsk carnallites: *Jour. Chem. Ind.* (Moscow) **5,** 1365–1369 (1928) cf. *Chem. Abstracts,* **23,** 3191 (1929).

METHODS FOR THE DETERMINATION OF BROMINE

The usual procedure in determining small amounts of iodine and bromine involve oxidizing the iodide and bromide to free iodine and bromine, extracting the free halogens with CS_2 or CCl_4, and matching the colors developed against a set of standards.

In the method of Lane,[6] 1:1 H_2SO_4 and chlorine water are used to oxidize the bromide to bromine. The amount of free bromine is measured in aqueous solution by a photoelectric colorimeter. The presence of iodine interferes with the determination. The quantities of solution used are unsatisfactory for the determination of bromine in saline minerals.

In the method adapted for natural brines by Sweeney and Withrow,[7] H_2SO_4 and chlorine water are used to liberate free bromine, which is extracted in CCl_4 and measured against standards, but no separate test for iodine is made. The quantities of brine and reagent used are unsatisfactory for analysis of bromine in saline minerals.

In the method of Harms[8] NaOCl is used to form free iodine from the iodide. After the iodine has been extracted in CS_2 or $CHCl_3$, an excess of NaOCl is added to form HIO_3 from I_2 and H_2SO_4 is added to liberate Br_2, which, if present, colors the CS_2 or $CHCl_3$ brown.

The method of Harms is the only procedure in which both iodine and bromine are determined. In the samples examined by the writer, it was necessary to test for iodine, though none was found in any of the samples. Therefore, a procedure adaptable to developing the iodine and bromine colors separately in saline minerals was worked out. Concentrated H_2SO_4, in contrast to NaOCl as in the method of Harms, is used to oxidize the iodide to free iodine. After the iodine is extracted and measured, chlorine water is added to oxidize the free iodine to iodate, and the bromide to bromine, which is then extracted in CS_2 and measured against standards prepared in the same way. In contrast to the large volumes used in the procedures of Sweeney and Withrow and of Lane, best results are obtained in this method, when volumes are kept to a minimum.

The following procedure is the one adopted: A one-gram sample of saline minerals is dissolved in 4 ml. of hot water, filtered into a test tube (1.5 cm. in diameter) through a 4 cm. filter paper, and washed once with 1 ml. of water.[9] Three ml. of concentrated H_2SO_4 are added, drop by drop,

[6] Lane, Marvin, Rapid estimation of bromides in the presence of chlorides: *Ind. Eng. Chem.*, Anal. Ed., **14**, 149 (1942).

[7] Sweeney, O. R., and Withrow, J. R., The chemical examination of natural brines: *Jour. Ind. Eng. Chem.*, **9**, 671–675 (1917).

[8] Harms, F., New method for detecting bromine and iodine: *Zeit. physik. chem. Unterricht*, **42**, 266–267 (1929).

[9] If the volume of the solution should be increased, the amount of H_2SO_4 added to

and the solution corked, shaken, and cooled. One ml. CCl_4 is then added, and the solution again shaken. Any iodine present will color the CCl_4 violet, and the iodine is determined colorimetrically.

The iodine is then oxidized to colorless iodate with chlorine water, and an excess of chlorine water is added to oxidize the bromide to bromine. The sample is then shaken to extract the bromine into the CCl_4 layer, and the amber color produced is matched against standards. It is necessary that the standards contain NaCl, since the presence of salt in the core samples tends to suppress the formation of free bromine.

The color of the CCl_4 layer varies with the concentration of chlorine water as well as that of bromine. Insufficient chlorine water does not oxidize all the bromide to free bromine; too much chlorine water oxidizes some of the bromine to bromate.

A series of standards 0.2 mg. apart from 0 to 2 mg. bromine in a gram of NaCl is prepared. The same quantity of strong chlorine water is added to the standards and to the unknowns. The strength of chlorine water chosen develops maximum color in the top range, but oxidizes some of the bromine to colorless bromate in the lower range. After a rough approximation of the bromine content has thus been made, a set of standards 0.1 mg. apart in the range of the unknown is prepared, and the strength of the chlorine water causing maximum depth of color is used in both standard and unknown.

If iodine is present in the unknown, a similar amount should be added to the standard. One-half gram samples should be used instead of gram samples for concentrations above 1.5 mg. of bromine. Results may be duplicated to 0.01% below 0.15% and to 0.02% between 0.15% and 0.30%.

Discussion of Results

The cores from Utah were analyzed for potassium, magnesium, and bromine, and the results tabulated in Table 1 as K_2O, MgO, and Br. Column *A* gives the total per cent of Mg computed to MgO found by chemical analysis. Column *B* gives the per cent of kieserite found by counting grains. Column *C* represents the per cent of MgO in kieserite, calculated from *B*. Column *D* contains the MgO equivalent in carnallite (*A–C*), and column *E* the per cent carnallite calculated from *D*. Column *F* contains the equivalent K_2O in carnallite, calculated from *E*, and column *G* the K calculated to K_2O found by chemical analysis. The

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oxidize iodide to iodine would have to be increased a corresponding amount. However, if it is unnecessary to test for iodine and if the KCl content is very high, the sulfuric acid added in the following step may be reduced to 1 ml. to prevent precipitation of K_2SO_4.

TABLE 1.—BROMINE CONTENT OF POTASH CORES FROM UTAH

Depth		A	B	C	D	E	F	G	H	I	J	K
		MgO equivalent to Mg (Chem. analyses)	% Kieserite (Counting grains)	MgO in kieserite (Calcd. from B)	MgO equivalent to Mg in carnallite (A–C)	% Carnallite to 1% (Calcd. from D)	Equivalent K_2O (Calcd. from E)	K_2O equivalent to K (Chem. analyses)	Difference K_2O (G–F)	% Sylvite to 1% (Calcd. from H)	% Carnallite+Sylvite (E+I)	% Bromine
McC	4658′ 3″–4660′ 1″	11.85	—	—	11.85	82	13.90	13.89	0	0	82	.24
W	4240′ 0″–4244′ 3″	12.52	—	—	12.52	87	14.75	14.81	.06	0	87	.24
W	4232′ 9″–4236′ 5″	8.50	—	—	8.50	59	10.00	16.10	6.10	10	69	.20
W	4245′ 0″–4246′ 9″	9.30	—	—	9.30	65	11.02	13.19	2.17	3	68	.18
McC	4631′ 4″–4635′10″	7.56	—	—	7.56	52	8.82	11.00	2.18	3	55	.16
W	4170′ 0″–4176′ 0″	6.42	—	—	6.42	45	7.63	7.86	.23	0	45	.12
W	4951′ 6″–4954′ 1″	.00	—	—	.00	0	0	26.60	26.60	42	42	.11
McC	4678′11″–4686′ 0″	.08	—	—	.08	0	0	25.25	25.25	40	40	.11
McC	4947′ 7″–4950′10″	4.86	—	—	4.46	31	5.18	6.26	1.08	2	33	.09
W	4149′ 9″–4152′10″	4.86	1	.29	4.57	32	5.43	5.39	.00	0	32	.09
W	4155′ 3″–4158′ 7″	4.94	—	—	4.94	34	5.77	6.14	.37	1	35	.09
McC	4630′ 4″–4631′ 4″	1.07	—	—	1.07	8	1.36	9.83	8.47	13	21	.07
McC	4964′ 0″–4966′ 2″	2.61	—	—	2.61	18	3.05	3.63	.58	1	19	.07
McC	4466′10″–4468′ 8″	1.82	—	—	1.82	12	2.03	7.63	5.60	9	21	.06
McC	4657′ 5″–4658′ 3″	.74	—	—	.74	5	.85	8.56	7.71	12	17	.06
W	4141′ 3″–4144′ 3″	2.35	1	.29	2.06	15	2.54	3.00	.46	1	16	.06
W	4158′ 7″–4159′ 7″	8.59	25	7.25	1.34	9	1.52	6.84	5.32	9	18	.06
W	4631′ 6″–4633′ 2″	.01	—	—	.01	0	0	14.60	14.60	23	23	.06
W	4954′ 1″–4956′ 3″	.00	—	—	.00	0	0	9.56	9.56	15	15	.06
McC	4419′ 9″–4421′ 9″	.02	—	—	.02	0	0	10.19	10.19	16	16	.05
McC	4672′ 0″–4678′11″	.03	—	—	.03	0	0	10.92	10.92	17	17	.05
W	4152′10″–4155′ 3″	1.75	—	—	1.75	12	2.03	2.38	.35	1	13	.05
W	4249′ 2″–4245′ 0″	.28	—	—	.28	2	.34	7.63	7.29	12	14	.05
McC	4660′ 1″–4661′10″	.12	—	—	.12	1	.15	9.14	8.99	14	15	.04
McC	4654′11″–4656′ 9″	.02	—	—	.02	0	0	11.20	11.20	18	18	.04
W	4161′ 6″–4163′ 0″	1.15	3.5	1.02	.13	1	.17	4.93	4.76	8	9	.04
W	4655′ 7″–4658′ 3″	.00	—	—	.00	0	0	14.89	14.89	23	23	.04
W	4658′ 3″–4659′ 6″	.00	—	—	.00	0	0	8.43	8.43	13	13	.04
W	4697′ 9″–4703′ 3″	.00	—	—	.00	0	0	6.60	6.60	10	10	.04
McC	4448′ 6″–4450′ 6″	.13	—	—	.13	1	.16	5.22	5.06	8	9	.03
McC	4661′ 1″–4666′ 8″	.06	—	—	.06	0	0	4.19	4.19	7	7	.03
W	4507′ 4″–4509′ 0″	.01	—	—	.01	0	0	7.96	7.96	12	12	.03
W	4550′ 0″–4554′ 8″	.00	—	—	.00	0	0	8.53	8.53	14	14	.03

difference in K_2O ($G-F$) is listed in column H, and the sylvite content, calculated from H, is given in column I. Total carnallite+sylvite is given in column J ($E+I$). The per cent bromine is given in column K. Results are arranged in order of decreasing bromine content.

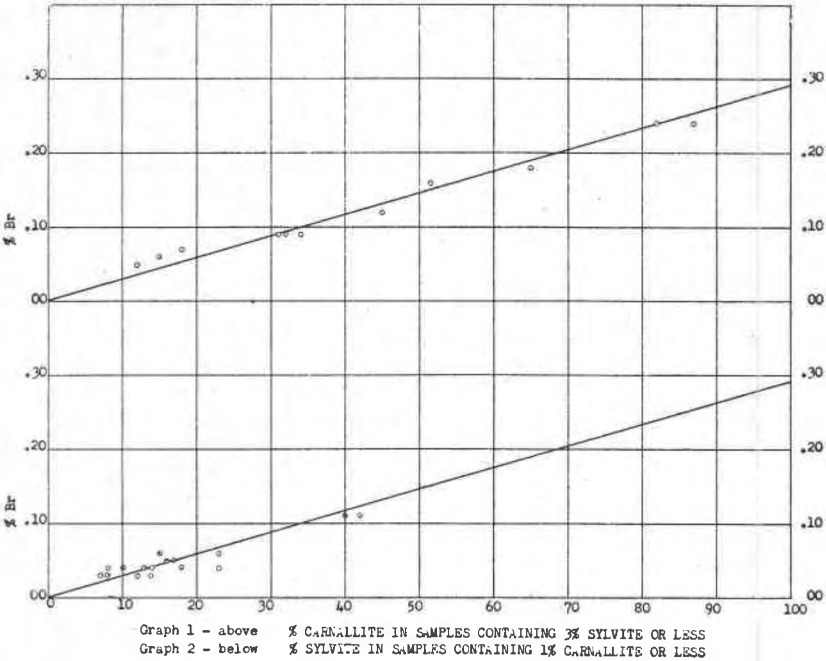

FIG. 1. Bromine content of carnallite and of sylvite from Utah.

The results from Table 1 are presented in Figs. 1 and 2, graphs 1, 2 and 3. In graph 1, the per cent of carnallite in samples containing 3% or less of sylvite is plotted against the bromine content. In graph 2, the per cent of sylvite in samples containing 1% carnallite or less is plotted against the bromine content. In graph 3, the total carnallite plus sylvite (column J, Table 1) is plotted against the bromine content. Six samples that are not included in graphs 1 and 2 are included in graph 3. Some of the values in graph 3 are not identical with those in graphs 1 and 2, since the former contains the sum of both carnallite and sylvite, while the latter contains only one mineral plotted against the bromine content.

To obtain a bromine value for 100% carnallite plus sylvite, the average carnallite plus sylvite content was obtained from column J, Table 1, and the average bromine content from column K, Table 1. The values were computed to 100% carnallite plus sylvite, giving .3% (.29%) bromine. A straight line was drawn from the origin to 100% carnallite plus sylvite—.29% bromine in graph 3. This line was superimposed on graphs 1 and 2. The positions of the points in respect to the line in graphs 1 and 2 definitely show that bromine is equally distributed between carnallite and sylvite, and for every 10% of carnallite plus sylvite, or of carnallite or sylvite alone, the bromine content increases .03% in these

TABLE 2. BROMINE CONTENT OF FOUR NEW MEXICO CORES*

Well and depth		Carnallite	Sylvite	Carnallite +Sylvite	Bromine
B M 8	630′6″–630′10″	55	11	66	.06
B M 8	563′0″–565′6″	53	—	53	.05
B M 15	650′3″–653′0″	60	—	60	.05
B M 14	659′9″–667′4″	5	36	41	.04
B M 15	653′0″–655′4″	53	—	53	.04
B M 8	710′11″–712′0″	1	34	35	.03
B M 14	621′0″–622′4″	3	30	33	.03
B M 15	609′6″–611′0″	8	32	40	.03
B M 16	508′0″–509′5″	3	30	33	.03
B M 16	515′7″–516′7″	—	32	32	.03
B M 8	627′3″–629′8″	3	17	20	.02
B M 8	642′5″–642′11″	1	18	19	.02
B M 8	645′6″–648′8″	2	19	21	.02
B M 8	743′0″–744′4″	—	31	31	.02
B M 14	656′0″–658′0″	20	4	24	.02
B M 14	658′0″–659′9″	15	2	17	.02
B M 15	611′0″–613′5″	10	3	13	.02
B M 8	563′6″–657′0″	8	—	8	.01
B M 8	625′7″–627′3″	9	—	9	.01
B M 8	629′9″–630′6″	10	4	14	.01
B M 8	630′10″–634′3″	2	5	7	.01
B M 8	708′0″–710′11″	1	7	8	.01
B M 8	712′0″–716′0″	1	9	10	.01
B M 14	617′0″–619′9″	1	5	6	.01
B M 14	622′4″–625′6″	6	2	8	.01
B M 15	648′1″–650′3″	1	9	10	.01
B M 16	506′0″–508′0″	—	8	8	.01
B M 16	516′7″–519′4″*	2	5	7	.01

* 26 additional samples from various depths containing between 0 and 6% carnallite plus sylvite, contained a trace of bromine.

two cores. The bromine content of these two wells may be closely approximated if the carnallite and sylvite contents are known.

In the cores from New Mexico are several potassium and magnesium minerals namely, carnallite, kainite, kieserite, polyhalite, and sylvite. The relative proportions of each were found by counting grains of crushed core and allotting the per cent potash found by chemical analysis to the various potash minerals.

Four cores drilled by the Bureau of Mines in New Mexico (holes B M 8, 14, 15, and 16) were analyzed for bromine and the results arranged in Table 2 in order of decreasing bromine content. The percentage of carnallite and of sylvite and of carnallite plus sylvite is tabulated. The values are then plotted in Fig. 2, graph 4. The carnallite-plus-sylvite content and the bromine content were averaged and the bromine value .1% (.093%) obtained by computing to 100% the sum of the carnallite and the sylvite. A straight line was drawn from the origin to 0.093% bromine, and 100% carnallite plus sylvite. The bromine content increases 1% (.093%) for every 10% carnallite plus sylvite in these four New Mexico cores.

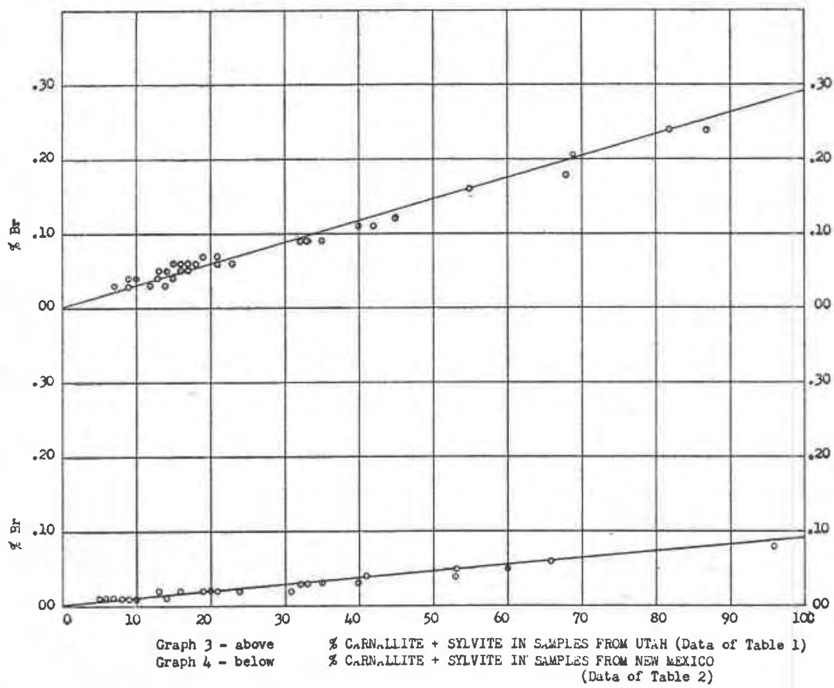

FIG. 2. Bromine content of carnallite plus sylvite, Utah and New Mexico.

No bromine was found in selected samples of apricot halite, blue halite, clear halite, gray anhydrite, and pink polyhalite from the U. S. Potash Company shaft no. 1, Eddy County, New Mexico, nor was any bromine found in långbeinite from shaft no. 2. A sample containing 96% sylvite from shaft no. 1 contained .08% bromine, while the four inch seam of milky white sylvite from bed no. 2 contained .07% bromine. Samples with varying amounts of carnallite contained from .04 to .07% bromine.

Bromine was determined on a sample of pure carnallite analyzed by J. J. Fahey,[10] from Government hole no. 1, Sec. 13, T. 17 S., R. 31 E., depth 933′6″, Eddy County, New Mexico, and .12% bromine was found.

From 1931 to June 1945 four and a half million tons of potash have been mined from the Permian basin. Most of the potash occurs in the mineral sylvite, although some carnallite, långbeinite, and polyhalite may have been included. Computing the tonnage of K_2O to KCl, it is found that 7 million tons of sylvite was mined during this period. On the assumption that sylvite from New Mexico contains .1% bromine, 7,000 tons of bromine was present in potash salts mined from the Permian basin during the period 1931 to 1945.

[10] Schaller, W. T. and Henderson, E. P., Mineralogy of drill cores from the potash field of New Mexico and Texas: U. S. Dept. Interior, *Geol. Survey, Bull.* **833,** 23 (1932).