

PHILOSOPHICAL TRANSACTIONS.

XVII. *Memoir on the occurrence of Iodine and Bromine in certain Mineral Waters of South Britain.* By CHARLES DAUBENY, M.D. F.R.S. Professor of Chemistry in the University of Oxford.

Read May 6, 1830.

THE discovery in sea-water of iodine and bromine, two principles which, although in minute proportions, are said to be generally diffused throughout the present ocean, naturally suggested the inquiry, as to whether these same ingredients might not be found to exist in springs occurring in inland situations when containing a similar saline impregnation. This accordingly has been already determined by STROMEYER, LIEBIG, and others, to be the case in many of the brine-springs of Germany, France, and Italy; but at the time my attention was first directed to the subject, I was unacquainted with any trials of the kind having been instituted with reference to those of this country, except by Professor TURNER of the London University, regarding the presence of iodine in the mineral waters of Scotland; in only one of which, that of Bonnington near Leith, he appears to have detected it. I was therefore induced in the course of last spring and summer to undertake a pretty extensive survey of such English springs as are known to contain a considerable proportion of common salt; and having succeeded in detecting in several of them traces of one or both the substances alluded to, I inserted a brief account of the results obtained, in the Philosophical Magazine and Annals of Philosophy for September last.

An article that has appeared in a subsequent number of the same periodical work has, however, been the means of drawing my attention to a little work

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by Mr. MURRAY, entitled "Experiments on Chemical Philosophy," which had not before fallen in my way; and from this it is clear, that the detection of iodine in the Gloucester Spa water had been made by that gentleman some time before I had engaged in the inquiry. I am unable, however, to discover in his publication, although it bears so late a date as 1828, any thing that can substantiate the assertion which its author has made in the number of the *Philosophical Magazine and Annals* referred to, as to his having anticipated me in the discovery of iodine in the springs at Cheltenham*, or in that of bromine in those of Ingestrie. I consider myself, therefore, still warranted in claiming as my own the first public announcement of the existence of bromine in our English springs; but I am far from attaching importance to a discovery which had been previously made in so many similar situations abroad, and would wish it to be understood, that my only pretence for offering to the Royal Society the present communication, is the circumstance of my having examined on the spot most of the mineral springs hereafter enumerated, and having undertaken, wherever it appeared practicable, to obtain an approximation at least to the proportion which these principles bore to the other ingredients present, and to estimate their comparative frequency and abundance in the several rock-formations.

To the geologist, the results of such an inquiry may be of interest, as tending to identify the products of the ancient seas in their most minute particulars with those of the present ocean: and to the physician it may be an object of curiosity, to speculate how far the unexplained virtues attributed to certain mineral waters depend on the presence of these ingredients, the energy of whose action may perhaps compensate for the minute quantity in which they are found. I confess, indeed, that with regard to the former of them, Iodine, we ought to be sceptical as to any medicinal agency that can be exerted by so small a quantity as a single grain diffused through ten gallons of water, the largest proportion in which I have ever detected it. But with respect to the second, Bromine, after considering the statements of its discoverer M. BALARD, as to its highly poisonous operation upon animals, which my own experience

* Mr. AINSWORTH, however, one of the editors of the *Edinburgh Journal of Natural and Geographical Science*, states, that he had communicated the fact of the existence of iodine in the Cheltenham waters previously to my announcement of it.

of the irritating effects of its vapour tends fully to confirm, I cannot view it as absurd to trace the medical virtues ascribed to such waters as those of Ashby-de-la-Zouch, to the presence of even so small a quantity as a grain of hydrobromate of magnesia (if such be the combination) in each pint of the water; and that the proportion would not fall far short of that, my experiments on this particular spring seem to warrant me in concluding. It is curious at least, that almost the only two brine-springs, properly so called, which have acquired any reputation as medicinal agents, that of Kreutznach in the Palatinate, and that of Ashby-de-la-Zouch in Leicestershire, both should contain a larger proportion than common of this new principle; and that in either instance that reputation should have been enjoyed, long before any suspicion as to their peculiar nature could have been entertained.

The objects I had in view in this inquiry being what are above stated, I have chosen to classify the springs noticed in the accompanying Table according to the geological position of the strata from which they issue; and under the head of each have set down the total amount of their saline ingredients; the nature and proportion of them as ascertained by former chemists, or, whenever I could not depend upon the results, by myself; and the proportion which the iodine and bromine, where either of these principles existed, bore to the quantity of water, and likewise to that of the chlorine which the solid ingredients of the spring might contain. The latter statement has been introduced in order to remove an impression which may have been created in consequence of the detection of iodine, as it is said, even in common pump-water*, when very large quantities of it were evaporated; from which circumstance it might be inferred, that this principle is not only a constant accompaniment of common salt, but that its quantity bears a pretty regular ratio to that of the latter ingredient. Although I have myself evaporated no less than forty-eight gallons of the Oxford pump-water without finding the slightest trace of iodine in the last portions, I shall not dispute the truth of the former position, which might possibly have been borne out, had still larger quantities been operated upon†; but that the latter opinion is untenable, will be readily seen from the

* Mr. CUFF, a chemist at Bath, has also detected it in the hot springs of that place, by evaporating about thirty gallons of the water.

† I am also loth to question the fact (stated on good authority) of the existence of a minute pro-

accompanying Table, which shows that the proportion of iodine to chlorine varies in every possible degree, and that the springs most strongly impregnated with common salt are in some instances those in which I have evaporated the largest quantity without detecting any trace of iodine. The same remark will equally apply to bromine ; so that the general inference seems to be, that although these two principles may perhaps be never entirely absent where the muriates occur, yet that their distribution is certainly very unequal, and therefore forms a proper subject of scientific research. The quantity in which the former of these ingredients occurs in mineral waters is commonly so inconsiderable, that I have been unable to determine it by direct analysis, and have been therefore obliged to content myself with obtaining an approximation to its real amount. In the case of one of the Leamington springs, indeed, I employed the agency of nitrate of silver to precipitate the iodine from the concentrated water, and afterwards separated by means of ammonia the chloride from the iodide of silver obtained. I have reason, however, to believe, from some comparative experiments, that where the proportion which this latter ingredient bears to the former one is extremely small, it may be taken up either wholly or in part by ammonia ; and I therefore contented myself in other instances with evaporating the water until it began to produce the characteristic blue or violet tinge with starch and sulphuric acid. This was then compared with the colour imparted by the same test to a solution of hydriodate of potass of known strength ; and the latter, if not of the same shade already, was brought to it by dilution with a measured quantity of water. Having thus noted the proportion of iodine in the test liquor with which the concentrated solution corresponded, it was easy to calculate what it must have been in the mineral water itself, by knowing the number of times its original quantity had been reduced by evaporation previously to the employment of this re-agent.

The sulphates and muriates present in brine-springs do not appear to interfere with the delicacy of this test ; but where bromine was also present, I have portion of iodine in sea-water, although I have reduced ten gallons of it, taken from the English Channel near Cowes, to less than half an ounce, without being able to detect any in the residuum. There seems reason, however, to infer, from what is stated in the next page, that the starch test cannot be relied upon to detect very minute quantities of iodine, when a comparatively large proportion of bromine is present in the same solution.

seen the liquor, either at the time or shortly after the operation of the re-agent, assume a pinkish hue, owing, as I suppose, to the reddish tinge of the bromine given out mixing with the blue colour of the iodide of starch. In stating therefore, as I have done in the Table, the proportions of iodine in several of the waters, I am far from pretending to offer more than an approximation to the relative quantity in which it occurs, and am fully aware of the necessity of more precise experiments, conducted on a different principle, before the points in question can be considered as satisfactorily determined.

The starch test I find will readily indicate a quantity of iodine not exceeding one grain to 7 gallons of water, or one 450,000th part; but as in no case that has occurred to me the proportion exceeded one grain to 10 or 12 gallons, and in many appeared scarcely to amount to one-10th of that quantity, I despaired of arriving at more accurate results, by adopting any other method that aspired to greater precision than the one already stated.

In every case in which I have noted that no iodine could be detected, the water had been concentrated at least as far as to one-30th of its original quantity without effect; so that the proportion of this principle, supposing after all any of it to exist, could not well amount to a grain in 200 gallons. In some cases, indeed, where the spring was one of weak impregnation, I have carried the concentration much further, as may be seen in the Llandrindod waters, where no traces of iodine appeared, until they had been reduced to nearly one-50th of their original volume.

In my trials for bromine, I have in great measure conformed to the directions of BALARD; first boiling down the water to about a fourth of its original quantity with a portion of quicklime to prevent the bromine from being dissipated by the heat; and then, after filtering the residuum, introducing chlorine as long as any sensible yellowness was caused by its addition. The water was then strongly agitated with ether, which collects on the surface, carrying with it the bromine with which it had combined, and was then poured off into a separate vessel. [The bromine, immediately upon being thus removed from the water, was treated with a quantity of a concentrated solution of pure soda sufficient to render the ether containing it colourless; the latter alkali being employed for this purpose in preference to the vegetable one, as I found that bromine formed with sodium a salt more soluble in alcohol than it did with potassium.]

Unfortunately, however, the salts which are contained in or deposited from the ethereal solution after the addition of the soda, appear to be of a very mixed description, consisting not only of the hydrobromate and bromate of soda, but also of the muriate and chlorate, together with a little uncombined alkali, if the proportion of the sodium to the bromine is not very nicely adjusted. I therefore began by heating the whole product sufficiently to convert the bromate of soda into the bromide, and the chlorate into the chloride, of sodium; and afterwards, in order to ensure the union of any alkali which may have been in excess with carbonic acid, I dissolved the whole in water impregnated with that gas. The solution was then brought to dryness, and strong alcohol added to separate the bromide of sodium as much as possible from the other ingredients; after which, the alcoholic solution, having been evaporated, was re-dissolved in water, and nitrate of silver added to it in order to form the insoluble bromide of silver, the weight of which, when dried and melted, would determine that of the bromine present, every 100 grains according to M. BALARD indicating 41.1 of this principle.

From the weight of the precipitate, however, I felt myself obliged to make a large deduction, in proportion to the quantity of alcohol employed, for the chloride of sodium at the same time taken up; having ascertained by a previous experiment how much common salt a given quantity of this menstruum could dissolve. The latter part of the process, however, being liable to some uncertainty, I should have preferred, had my engagements permitted, re-examining the waters on the spot, and operating on such quantities of them as would have enabled me to extract appreciable quantities of bromine. This indeed I have done in the case of the Middlewich water, but not with sufficient attention to the quantities employed and obtained, to enable me to calculate in this manner the exact proportions between them: with regard to the other springs, the quantity of water which I could conveniently transport to my laboratory was not such as to enable me to pursue with much hope of success this particular method. It is therefore with diffidence that I offer provisionally the statements given in the Table, as an approximation to the relative quantities of bromine existing in some of our English springs, calculated according to the scheme of analysis above stated; and shall hope at some future and not very distant period to obtain results more worthy of reliance, should my

further labours on this subject not be rendered in the mean time unnecessary by the investigations of some other chemist. In cases where the quantity of this principle appeared to be less considerable, as in the Leamington, Cheltenham, and Gloucester waters, I have contented myself with guessing at its proportion by concentrating the water until it assumed a decidedly yellow tinge with chlorine, noting what proportion of bromine in water produced a colour of equal intensity.

The earliest of the rock-formations in this country that come under our consideration with reference to the present inquiry, is the greywacke slate of North Wales, which in the neighbourhood of Bualt in Radnorshire gives out springs containing a notable proportion of common salt. Those of Llandrindod have long enjoyed some reputation as medicinal agents, but their composition does not appear to have been correctly ascertained; for the most modern analysis I have seen* assigns to them a considerable proportion of muriate of magnesia, of which I find scarcely a trace. The more newly discovered springs at Bualt itself, though less celebrated, are similar in point of constitution; and being double the strength of those of Llandrindod, ought to possess superior medical virtues. At both places are waters which differ from the rest in containing an unimportant impregnation of sulphuretted hydrogen, but in other respects correspond.

Many of our coal-pits emit streams of salt water; but the most remarkable spring of the kind is that already noticed, of Ashby-de-la-Zouch in Leicestershire, which for the last few years, especially since the erection of the baths, which are now so great an ornament to the spot, has acquired a certain local reputation in the cure of diseases. Previously to the discovery of bromine, of which I detected in this water an appreciable quantity, Dr. THOMSON of Glasgow had examined its composition; and I have therefore been satisfied with adhering to the results of his analysis, which is stated in the Table.

The most important, however, of the salt-springs that we meet with in this country are those in the new red sandstone formation of Cheshire; for an analysis of which I may refer to a paper of Dr. HENRY's, published in the Transactions of this Society. In this instance, also, I have adopted the statements of another, merely making a proportionate deduction from the amount

* Analysis of the Llandrindod Waters; by Mr. WILLIAMS, Surgeon, 1819.

of the ingredients given by that able chemist, in consequence of the weaker impregnation of the samples of water I employed, than of those on which he appears to have operated.

It will be seen by reference to the Table, that all the brine-springs of that district contain bromine, and most of them iodine ; indeed it is probable that if I had had time to concentrate larger quantities of the water, the latter would have been detected throughout. It may be remarked, however, that the rock-salt of Northwich in Cheshire contains no trace of either principle ; a circumstance explicable from the more deliquescent nature of the hydriodic and hydrobromic salts, which would cause them, together with the earthy muriates, to remain in the mother-liquor after the common salt had crystallized, and thus to become distributed through the substance of the marly beds afterwards formed over the rock-salt, from which the brine-springs appear to derive their saline impregnation.

There is a blue variety of rock-salt met with at Ischel near Saltzburg, which, from the resemblance between its colouring matter and that of the compound of starch and iodine, might be suspected to contain this latter principle united with some kind of vegetable matter. I have been unable to obtain a specimen deeply enough tinged with the colouring matter alluded to, to set the question completely at rest ; but on dissolving a portion of the blue salt, which I obtained through the kindness of Mr. HEULAND, in water, not the slightest tinge appeared to be communicated to the solution, neither did any blueness appear on re-crystallizing the salt. The specimen alluded to gave no indications of iodine when tested with starch in the usual manner, and was nearly pure from admixture with foreign ingredients, although it appeared to contain a trace of sulphuric acid and of lime. At present, therefore, I am inclined to attribute the colour rather to some peculiar arrangement of the particles of the common salt itself, than to the presence of any other ingredient.

The springs containing purgative salts, which arise from the lias clay in various places along its whole range from Leamington to Gloucester, appear to be derived from the same source as the brine-springs of Cheshire and Worcestershire above alluded to ; but their saline contents have been modified by the sulphuric acid generated by the decomposition of the sulphuret of iron present in the stratum from which they immediately proceed. Hence the pro-

portion of earthy muriates is usually greater in them than in the brine-springs properly so called ; because the muriatic acid disengaged by the action of the sulphuric acid upon the common salt has dissolved a fresh quantity of lime or magnesia from the surrounding materials of the rock.

If such be the origin of the sulphates of soda and magnesia which impart to these waters their aperient quality, it would be natural to expect that they should be found in greater abundance on the first discovery of the spring than after it has been long drawn upon ; and hence, perhaps, the remarkable discrepancy between the results of my examination of the Gloucester and some other waters, and those given on the authority of former chemists, may be explained, without impeaching the accuracy of either.

It will be seen by reference to the Table, that I have represented the ingredients of the Leamington waters on the authority of Dr. THOMSON, as stated by Dr. LOUDON in his *Practical Dissertation** on these springs ; and those of Cheltenham, with the exception of one lately discovered at Pittville, on that of Dr. SCUDAMORE. The springs of Tewkesbury and Gloucester I have myself examined ; there being of the former no analysis at all, and of the latter only one by Mr. ACCUM, which I had reason to believe, what I in fact found, quite inapplicable to its present composition. The spring which goes by the name of the Chalybeate Saline is at present destitute of iron, which I am assured it formerly possessed, whilst the Sulphureous contains no trace of sulphuretted hydrogen. These two springs, which at present appear almost identical, are the ones most strongly impregnated with purgative salts, and therefore approximate more nearly to the character of that analysed by Mr. ACCUM, according to his representation, than either of those termed “the pure saline,” which he professed to have examined. Many of these springs it will be seen contain traces of bromine and iodine ; but they seem to be less common in the aperient waters which are occasionally met with in the chalk and tertiary districts of this country ; for I have examined three—those, namely, of Epsom, of Chad’s Well in Gray’s-Inn Lane, and of St. Leonard’s Hill near Windsor, without discovering traces of iodine in any one. In the Epsom water alone a slight trace of bromine was perceptible.

With regard to the state of combination in which these principles occur, I

* Leamington, 1828.

have only to observe, that they are no doubt combined with hydrogen, forming the hydriodic and hydrobromic acids, and neutralized in all probability by magnesia, both forming with this basis salts decomposable at a low temperature, which seems to be the case with the compounds of both bromine and iodine existing in the waters I have examined. Even long continued boiling, there is reason to believe, diminishes the quantity of bromine originally present ; and hence it seems advisable, when the object is to estimate the whole of this principle which a mineral water may contain, to combine the hydrobromic acid with lime, in the manner which I have recommended to be done when speaking of the mode of separating bromine from its combination.

I may conclude by observing, that there is little question as to the possibility of procuring a sufficient supply of bromine from our English brine-springs, should a demand be created for this new substance, either for medical purposes or for the arts of life ; for, from a few rough trials of its comparative abundance in the Middlewich and Ashby springs, and in those of Kreutznach in the Palatinate, which affords, it is said, the principal supply for present consumption, I should regard our own quite as highly charged : neither can it be doubted but that the proportion of bromine present in many brine-springs exceeds considerably that contained in the present ocean, which, from experiments recently made by myself on water taken from the English Channel a short distance from Cowes, I have stated in the Table as existing in the proportion of one grain to the gallon.

TABLE comprehending a List of certain Springs in South Britain, which contain Common Salt in considerable quantity.

TABLE comprehending a List of certain Springs in South Britain, which contain com-
the other Ingredients

Geological Position.	Locality of the Spring.	Name of the Spring.	Total of its Saline Contents in the Pint.	Iodine.	
				Its proportion to The Water.	The Chlorine.
TRANSITION SLATES.	Llandrindod, Radnorshire.	No. 1. The Pure Saline.	31.35 Gr.	Seems not to exceed 1 Grain to 343 Gallons.	As 1 to 50.000
	Ditto	No. 2. The Chalybeate Saline.	Nearly as No. 1.	None detected.	————
	Bualt, Radnorshire.	No. 1. The Saline.	77.6 Gr.	A trace, nearly the same as that exhibited by No. 1. Llandrindod.	As 1 to 120.000
	Ditto	No. 2. Sulphuretted Saline.	Nearly as No. 1.	None detected.	————
	Ditto	No. 3. The Chalybeate Saline.	Nearly as No. 1.	None detected.	————
COAL FORMATION.	Ashby-de-la-Zouch, Leicestershire.	The Moira Brine Spring.	179.88 Gr.	None detected.	————
	Near Newcastle-upon-Tyne.	The Walker Colliery Brine Spring.	192.0 Gr.	None detected.	————
	Kingswood, near Bristol.	The Soundwell Colliery Brine Spring.	64.0 Gr.	None detected.	————
	Northwich, Cheshire.	Brine Spring.	1696 Gr.	None detected.	————
	Middlewich, Cheshire.	Ditto	1824 Gr.	A trace, probably not exceeding 1 Grain to 343 Gallons.	As 1 to 2.650.000
	Nantwich, Cheshire.	Ditto	1760 Gr.	1 Grain to about 12 Gallons.	As 1 to 96.000
	Wheelock, Cheshire.	Ditto	1440 Gr.	A trace, apparently not greater than that in the Middlewich.	Nearly as 1 to 2.000.000
	Droitwich, Worcestershire.	Ditto	1746 Gr.	None detected.	————
	Shirleywich, Staffordshire.	Ditto	1552 Gr.	None detected.	————
	Leamington, Warwickshire.	No. 1. Robbins's Well.	95.948 Gr.	1 Grain to about 10 Gallons.	As 1 to 3440
LIAS CLAY.	Ditto	No. 2. Royal Pump Saline Spring.	134.749	Rather less than in No. 1.	————
	Ditto	No. 3. Smith's Pump.	109.992	A trace, but apparently not more than a Grain to 192 Gallons.	As 1 to about 48.000
	Ditto	No. 4. Wise's Pump.	107.396	Nearly as the preceding.	————

mon Salt in considerable quantity; together with a Statement of the Proportion of this and present in a Pint of each.

Bromine.		Chlorides of			Sulphates of			Per-oxide of Iron.	Carbonates or other Salts.	Authority on which the Statement of the Saline Ingredients is given.
Its proportion to The Water.	The Chlorine.	Calcium.	Magnesium.	Sodium.	Lime.	Magnesia.	Soda.			
Not estimated, but a distinct trace.	Not estimated.	6.6	24.75							DAUBENY.
As No. 1.	————	Ingredients as No. 1. except that it contains					0.6			DAUBENY.
A trace, not estimated.	————	11.2	A trace	66.4						DAUBENY.
A trace, not estimated.	————	Ingredients nearly as No. 1.								DAUBENY.
A trace, not estimated.	————	Ingredients as No. 1. except that it contains					A trace			DAUBENY.
1 Gallon seems to contain 4.68 Grains.	As 1 to 180	36.4	3.72	133.0	4.24		2.52			THOMSON.
A trace, not estimated.	————	2.8	2.8	186.0						DAUBENY.
None detected.	————	2.5		58.5			3.0			DAUBENY.
1 Gallon seems to contain 1.2 Grains.	As 1 to 6600	0.42	1.27	1667.0	25.5				Insoluble matter 1.696	HENRY.
9.36 Grains of Brome in 1 Gallon.	As 1 to 860	0.5	1.37	1793	27.35				Insoluble matter 1.3	HENRY.
6.32 Grains of Brome in 1 Gallon.	As 1 to 1275	0.45	1.32	1730	26.5				Insoluble matter 1.76	HENRY.
A trace, not estimated.	————	0.36	1.1	1415	22.0				Insoluble matter 1.44	HENRY.
None detected.	————		A trace	1691			40.25			DAUBENY.
4.32 Grains of Brome to 1 Gallon.	As 1 to 1720	38.0	22.0	1490						DAUBENY.
1 Grain to about 10 Quarts.	As 1 to 430	23.5	8.468	35.35			28.619	A trace		THOMSON.
Nearly as strong as No. 1.	————	20.902	12.365	67.78			32.744	0.956		THOMSON.
A trace.	————	19.772	2.121	47.865			40.234	A trace		THOMSON.
A trace.	————	18.777	22.592	26.61			39.457	A trace		THOMSON.

Geological Position.	Locality of the Spring.	Name of the Spring.	Total of its Saline Contents in the Pint.	Iodine.	
				Its proportion to The Water.	The Chlorine.
LIAS CLAY.	Leamington, Warwickshire.	No. 5. Smart's Saline.	92.589	Nearly as the two preceding.	—
	Ditto	No. 6. Lord Aylesford's.	113.995	None detected.	—
	Ditto	No. 7. Reid's Sulphureous.	79.142	None detected.	—
	Ditto*	No. 8. Reid's Saline.	102.597	None detected.	—
	Gloucester.	No. 1. Sulphureous Saline.	84.2	About 1 Grain to 50 Gallons.	As 1 to 12,000
	Ditto	No. 2. Chalybeate Saline.	In all respects agrees with No. 1	in point of com	
	Ditto	No. 3. Strong Saline.	76.5	About 1 Grain to 96 Gallons.	As 1 to 33,000
	Ditto	No. 4. Weak Saline.	75.22	Nearly as No. 3.	—
	Tewksbury.	The Walton Spring.	46.1	About 1 Grain to 36 Gallons.	As 1 to 6690
	Cheltenham.	Pittville, No. 1. "The Pure Saline."	45.8	None detected.	—
	Ditto	Sherborne, No. 4.	84.44	About 1 Grain to 90 Gallons.	As 1 to 33,000
	Ditto	Thomson's, No. 4.	80.13	About 1 Grain to 30 Gallons.	As 1 to 3600
	Ditto	Old Well, No. 1.	81.51	About 1 Grain to 60 Gallons.	As 1 to 19,000
	Ditto*	Thomson's, No. 2.	52.29	None detected.	—
OOLITIC STRATA.	Melksham, Wiltshire.	The Saline Spring.	107.42	None detected.	—
CHALK FORMATION.	Epsom, Surry.	The Saline Spring.	33.2	None detected.	—
TERTIARY ROCKS.	Windsor.	St. Leonard's Hill Spring.		None detected.	—
	Gray's Inn Lane, London.	Chad's Well.		None detected.	—
PRESENT OCEAN.	Off Portsmouth.			None detected.	—

* In none of the remaining Cheltenham or Leamington Springs could I satisfy myself of the existence of either iodine or bromine.

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