THE CHEMICAL CHANGES WHICH OCCUR IN SAMPLES OF EXCRETALLY POLLUTED WATER UNDER CERTAIN SPECIFIED CONDITIONS.

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The chemical changes which occur in the dissolved solids of sewage on discharge into sea-water have been investigated by several workers (see references 1–11). Some observations on the difference of these changes to those occurring in polluted fresh water have been made by Letts and Richards(6, 11). In regard to waters whose saline composition is not such as to preclude their admissibility for potable purposes on this account, Liversidge(12) has made a brief communication on the variation in the free and albuminoid ammonia. His investigations, made nearly half a century ago, were under artificial conditions which do not simulate water examination practice.

In sea-water the salts act as antiseptics(4) and therefore the conditions in domestic water supplies are vitally different. The writer has made an extended research into the chemical changes which occur in samples of water, originally of potable quality, after pollution by excreta. In the present communication consideration is given to the results obtained under three conditions only. These were when the samples (*a*) were exposed to light; (*b*) contained metallic impurities; (*c*) were chlorinated.

The investigation was made with reference only to the detection of excretal pollution in potable waters, and the analytical determinations were therefore limited to the substances whose presence is indicative of such, *i.e.* free ammonia, albuminoid ammonia, nitrites, and nitrates.

The general principle of the research was the preparation of bulk quantities of polluted water which were then divided into samples of exactly similar original composition by filling into stoppered bottles. These were set aside, and analysed after various periods of storage. Details of these samples are given under the headings below.

SAMPLES EXPOSED TO LIGHT.

It has always been considered that on storage of water samples the chemical evidence of any excretal pollution is rapidly destroyed and that this change was greatly accelerated by exposure to light. Preceding research (not yet published) having disproved the alleged rapid destruction of evidence when the samples were stored in the dark it was desirable to investigate the effect of exposure to light.

Series C. In this series, to about 10 litres of water of good quality from a deep well in the chalk, about 5 c.c. of a fresh suspension of soil was added. The soil was obtained from the roots of growing turf. This mixture was then polluted with 5 c.c. of a suspension of faeces one day old and 1 c.c. of fresh urine; the whole was very thoroughly mixed and aerated by shaking. This was then filled into sixteen 500 c.c. stoppered bottles; eight were stored at room temperature in the light (C 1) and the other eight in the dark at a colder temperature (C 2). At various periods bottles from each storage space were simultaneously analysed. The results are summarised in Table I.

Table I. Series C.

Analytical results, after various periods of storage, of samples of polluted water of the same original composition; (1) *stored in light;* (2) *stored in dark. Parts per* 100,000.

	C 1, stored in light at room temperature			
Days stored	Average temperature of storage space to date of analysis	Free ammonia	Albuminoid ammonia	Nitrites
Before pollution	—	0·0004	0·0022	0·0001
Immediately after pollution	—	0·0126	0·0300	0·0001
1	15·9° C.	0·0132	0·0292	0·0001
6	15·6	0·0236	0·0216	0·0001
9	14·4	0·0260	0·0182	0·0001
13	14·4	0·0264	0·0172	0·0001
20	14·3	0·0300	0·0158	0·0020
30	15·0	0·0084	0·0160	0·0065
41	15·5	0·0002	0·0364	0·0700
51	15·8	0·0000	0·0652	0·0700
	C 2, stored in dark at a lower temperature			
Days stored	Average temperature of storage space to date of analysis	Free ammonia	Albuminoid ammonia	Nitrites
Before pollution	—	0·0004	0·0022	0·0001
Immediately after pollution	—	0·0128	0·0314	0·0001
1	13·9° C.	0·0131	0·0310	0·0001
6	12·5	0·0172	0·0206	0·0001
9	12·4	0·0284	0·0190	0·0001
13	12·2	0·0324	0·0176	0·0002
20	12·2	0·0300	0·0150	0·0020
30	12·2	0·0004	0·0134	0·0050
41	12·7	0·0004	0·0112	0·0600
51	12·7	0·0000	0·0098	0·0700

It will be seen that for all practical purposes there was no difference in the rate of production and amount of free ammonia and nitrites in C 1 and C 2 despite the samples in the light being maintained at a higher temperature. After the 20th day, however, while the albuminoid ammonia in the samples stored where light was excluded continued to decrease, in those stored in the light it enormously increased. These latter samples, after this period, showed a progressive development of a green sediment, which, on microscopical examination, was found to be algae. The addition to the albuminoid ammonia

caused by this is so great as to entirely vitiate the interpretation of the results of an analysis.

The contention, then, that water samples must be stored in the dark is confirmed but the reason for this is that otherwise there is a fallacious increment to, not a decrement of, the indications of pollution as is commonly supposed.

In another series stored in the light (Series D), growth of algae commenced as early as the 14th day; in no case did samples stored in the dark show growth of algae even after periods exceeding three months.

SAMPLES STORED IN THE DARK: EFFECT OF METALLIC IMPURITIES.

In view of the very great influence of minute quantities of metallic salts in water on its bacteriological content, demonstrated by E. L. Atkinson and the writer (13), a similar investigation was made of the effect on the chemical changes which take place in excretally polluted waters. This was the subject of Series H.

Series H. To 8 litres of ammonia-free distilled water, distilled from an all-glass apparatus, 1·2 c.c. of fresh suspension of soil was added and thoroughly mixed. The following day 0·4 c.c. urine and 0·3 gm. faeces in suspension were added. The whole was mixed and seven 500 c.c. bottles were filled. To the remaining quantity of polluted water there was added copper (as copper sulphate) to the extent of 0·1 part per 100,000, and mixed. Seven 500 c.c. bottles were then filled with this treated water. All the samples were stored in the dark under identical conditions and, at intervals, bottles of the original water ("control") and the treated water ("copper") were simultaneously examined for free ammonia, nitrites, and nitrates.

The results are summarised in Table II.

It is at once evident that the presence of minute quantities of certain metallic salts in polluted water can exert a very great influence on the chemical changes which take place and this must be an imperative consideration in interpreting the results of an analysis. In this series, 0·1 part of copper per 100,000 very greatly restrained the production of free ammonia and entirely inhibited its conversion into nitrites and nitrates. The creation of evidence of original pollution has therefore been, to a great extent, prevented. In the previous research quoted it was found that the most marked effect exerted by the four metals tested for in the routine examination of water was in the order—copper, zinc, lead, iron.

SAMPLES STORED IN THE DARK: EFFECT OF CHLORINATION.

Chlorination of water supplies is now so commonly employed for purification purposes that it was considered desirable to determine the influence of this addition of free chlorine on the chemical changes which normally take place in polluted water. This was the subject of the concluding experiments.

Table II. Series H.

Analytical results, after various periods of storage, of samples of polluted water of the same original composition; untreated (control); containing copper to the extent of 0·1 *part per* 100,000 (*copper*). *Parts per* 100,000.

Days stored	Average temperature of store to date of analysis	Control			Copper		
		Free ammonia	Nitrites	Nitrates	Free ammonia	Nitrites	Nitrates
Immediately after pollution	—	0·0078	0·0002	0·0040	0·0070	0·0002	0·0040
12	20·7° C.	0·0370	0·0002	0·0040	0·0160	0·0002	0·0040
24	21·8	0·0460	0·0008	0·0040	0·0228	0·0001	0·0040
35	22·0	0·0564	0·0090	0·0060	0·0264	0·0002	0·0040
47	22·5	0·0390	0·0150	0·0060	0·0280	0·0002	0·0040
59	23·3	0·0270	0·0002	0·0680	0·0280	0·0000	0·0040
70	23·6	0·0040	0·0000	0·2160	0·0296	0·0000	0·0040

Table III. Series Q, R, and S.

Analytical results, after various periods of storage, of samples of polluted water of the same original composition; untreated (Q); chlorinated to the extent of 0·75 *part per million* (*R*); *chlorinated to the extent of* 3·0 *parts per million* (*S*). *Parts per* 100,000.

Days stored	Average temperature of storage space to date	Free ammonia			Albuminoid ammonia			Nitrites			Nitrates		
		Q	R	S	Q	R	S	Q	R	S	Q	R	S
1	19·2° C.	0·0044	0·0096	0·0010	0·0216	0·0180	0·0102	0·0003	0·0001	0·0000	0·0040	0·0040	0·0040
10	18·9	0·0164	0·0068	0·0002	0·0060	0·0072	0·0092	0·0004	0·0001	0·0000	0·0040	0·0040	0·0040
17	15·8	0·0240	0·0068	0·0002	0·0180	0·0144	0·0102	0·0002	0·0001	0·0000	0·0040	0·0040	0·0040
24	15·4	0·0160	0·0064	0·0002	0·0036	0·0144	0·0084	0·0002	0·0001	0·0000	0·0040	0·0040	0·0040
30	15·3	0·0164	0·0052	0·0001	0·0088	0·0092	0·0064	0·0007	0·0001	0·0000	0·0080	0·0040	0·0040
35	15·2	0·0196	0·0080	0·0008	0·0096	0·0132	0·0088	0·0005	0·0001	0·0000	0·0080	0·0040	0·0040
42	15·2	0·0192	0·0076	0·0008	0·0052	0·0072	0·0080	0·0006	0·0001	0·0000	0·0080	0·0060	0·0040
50	15·5	0·0112	0·0080	0·0006	0·0080	0·0144	0·0096	0·0045	0·0001	0·0000	0·0080	0·0060	0·0040
62	15·4	0·0000	0·0108	0·0008	0·0064	0·0160	0·0088	0·0001	0·0001	0·0000	0·0080	0·0080	0·0060
66	15·5	—	—	—	—	—	—	0·0000	0·0001	0·0000	—	—	—
73	15·7	0·0000	0·0108	0·0012	0·0048	0·0148	0·0100	0·0000	0·0000	0·0000	0·0380	0·0120	0·0080

Series Q, R, and S. Six litres of ammonia-free water and 250 c.c. of a solution-suspension of mineral salts commonly present in natural potable waters were shaken together; the mineral salts mixture contained, in one litre, sodium chloride 2·25 gm., calcium chloride 7·50 gm., magnesium chloride 1·50 gm., calcium carbonate 0·75 gm., calcium sulphate 7·50 gm., and calcium oxide 2·25 gm. Then 50 c.c. of fresh soil suspension was added and the whole mixed. To this was further added 1·5 c.c. of urine and 30 c.c. of a suspension of faeces (5·15 gm. to 100 c.c.) and mixed by shaking after making to 7·5 litres. The suspended matter was allowed to settle completely overnight and next day six litres of the clear liquid was run off.

Series Q. One litre of the above polluted water was diluted with ammonia-free distilled water to 7·5 litres and mixed. This was filled into thirteen 500 c.c. stoppered bottles (control).

Series R. Prepared as Series Q and chlorinated in bulk to the extent of 0·75 part per million by the addition of free chlorine from a solution of bleaching powder, and subsequently filled into bottles as above.

Series S. As Series R but chlorinated to the extent of 3·0 parts per million.

All the samples were stored in the dark under identical conditions and at intervals bottles of the control and the treated waters were simultaneously examined for free ammonia, albuminoid ammonia, nitrites, and nitrates. The results obtained are summarised in Table III.

The influence of the addition of minute quantities of free chlorine on all four substances determined is strikingly manifest and the question of chlorination must be a further vital consideration in the interpretation of water analysis results. Chlorination to the extent of 3·0 parts per million completely prevented, for all practical purposes, the production of free ammonia, nitrites, and nitrates, *i.e.* it inhibited the formation of evidence of pollution and even one quarter of this amount was only slightly less effective.

Attention is drawn to the irregular amounts of albuminoid ammonia in the control samples and the effect of chlorination in very greatly reducing this variation. It was thought that the irregular results might be due to inaccuracy of the analytical process but this is not so as simultaneous determinations in triplicate made in other series (Series V 1, 2, 3) gave almost identical results, namely, 0·0160, 0·0162, and 0·0160 parts per 100,000 respectively.

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