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Sorption Behavior of Mercuric and Methylmercuric Salts on Wool

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Synopsis

Sorption by wool of mercuric nitrate, mercuric chloride, and methylmercuric chloride was measured by atomic absorption spectroscopy. Both inorganic mercury compounds are efficiently taken up at low concentrations from acid solution. The rate of binding from the nitrate is appreciably slower than from the chloride. Methylmercuric chloride is bound slowly at low pH, rapidly at pH 6. The extent of its binding is roughly 10% to 20% of that of the inorganic salts. The wool-bound mercury can be recovered by serial extraction with aqueous citrate or ethylenediaminetetraacetate at pH 6. The residual, firmly bound mercury is roughly equivalent to the sulfhydryl sulfur. Sorption of inorganic mercury compounds at low pH roughly follows a Freundlich isotherm in the concentration range 5×10^{-6} to $10^{-1}M$. Sorption of methylmercuric chloride at pH 6 follows a roughly parallel isotherm in the range 5×10^{-6} to $10^{-3}M$. These data suggest the potential value of wool and other animal keratins to remove and recover mercury from contaminated water. Wool may also serve as an instructive model for mercury binding and release in the body.

INTRODUCTION

Mercury pollution is currently receiving much attention. Although the danger of mercury to health has long been known, the problem was brought into focus recently when various coastal waters, lakes, and rivers were found dangerously polluted by industrial and agricultural activities. Microorganisms methylate mercury and its derivatives to methylmercury derivatives. In this form it concentrates as it moves through the food chain.

Several authors have considered the binding of mercury compounds by wool.[1-10] For example, Speakman and Coke[2] and Barr and Speakman[3] studied the uptake of mercuric chloride and acetate under various conditions, partly to find a less hazardous reagent to assist felt making. Hojo[4] found that alkali treatment of wool increased sorption of mercury more than for other metals and[5] that mercury has a lower activation energy for sorption than typical dyes. Binding of mercury compounds under specified conditions has been proposed to determine free sulfhydryl and disulfide groups in proteins.[6] Burley,[7] Burley and Horden,[8] Human,[9] and Leach[10] have

studied the binding of various mercury compounds to wool for analytical purposes.

Some characteristics that may give wool and other hairs special utility are (1) low solubility; (2) accessibility to water and solutes in aqueous media; (3) physical form, as crimped and resilient fibers with diameters of the order of 20 to 100 μm; (4) relatively high content of particular reactive groups (Table I) that may serve as binding sites for mercurials or that can be chemically modified to provide binding sites or a more favorable binding environment; and (5) variety and juxtaposition of reactive sites that may allow cooperative reaction to bind substances more effectively than by the different kinds of sites acting individually.

This paper describes measurements of absorption of $HgCl_2$, $HgNO_3$, and CH_3HgCl by wool from aqueous media. We surveyed binding of mercury (from mercuric chloride and methylmercuric chloride) by several agricultural products and, on wool, at various pH's from 2 to 11. Effects of time and concentration are recorded. Desorption of mercury from wool is possible with several reagents. These results are presented as a basis for possible use of wool (for example, wool waste) or other animal hairs to remove and recover mercurials from industrial process effluents and contaminated waters. A preliminary report of part of this material has been published.[1]

EXPERIMENTAL

Adsorption

The wool used was a fine top (Dubois, Idaho, 1961 clip) with measured moisture content 10.5% of weight taken. Initial tests were made with wool that had been extracted with alcohol and ether, but extraction was discontinued when it was found to have no effect. Solution (150 ml) containing a measured amount of mercury compound was put into a 250-ml Erlenmeyer flask. Wool (1.50 g = 1.35 g dry weight) was added and the flask shaken for a measured time at 21°C. Sorption of $HgCl_2$ and CH_3HgCl by miscellaneous agricultural products was surveyed under the same conditions.

Reduced Wool

Wool was reduced by treating 10 g with 4 ml of tri-*n*-butylphosphine[11] in a mixture of pH 7.8 Tris buffer and *n*-propanol (1:1 by volume), shaking for one day under nitrogen. The liquid to wool ratio was 75:1.

Analysis

Mercury down to about 0.5 ppm was determined by specific atomic absorption with a Perkin-Elmer Model 303 spectrometer equipped with an acetylene–air burner. A few measurements at lower concentrations were made by a flameless method in which mercury in aqueous solution

TABLE I
Reactive Groups in Wool

Kind[a]	Concentration, moles/kg
Peptide (secondary amide)	8.8
Aliphatic hydroxyl	1.47
Half-disulfide	0.86
Total base	0.86
arginine	0.55
lysine	0.22
histidine	0.07
terminal amine	0.02
Free carboxyl	0.84
Primary amide	0.76
Phenolic hydroxyl	0.29
Tryptophan	0.04
Methionine	0.04
Sulfhydryl	0.04

[a] The disulfide content is variable and can be influenced by nutrition and weathering. The carboxyl content can be increased at the expense of primary amide by hydrolysis. The sulfhydryl content can be increased by copper deficiency in the diet and is also affected by weathering.

was reduced by stannous chloride and its vapor aspirated through a 10-cm quartz cell. Standard solutions were prepared in media similar in composition to those being analyzed.

Desorption

Two separate lots of wool with adsorbed mercury were used. The first (Hg-wool A) was made by shaking 7.5 g of wool in 750 ml of 0.01*M* $HgCl_2$, pH about 2.5, for 20 hr; it was then washed three times with distilled water and air dried at room temperature. It contained 46 mg of mercury per gram of wool. This lot was used to survey effects of pH.

The second lot (Hg-wool B) was made similarly except that 0.1*M* $HgCl_2$, pH about 1.5, was used. In this case the wool was cut into short pieces to aid uniformity, shaking was continued for 60 hr, and the wool was not rinsed; excess liquid was absorbed by pressing between filter papers. This lot contained 160 mg of mercury per gram of wool. It was used to study desorption by solutions of various mercury binding reagents.

To measure desorption, 0.5-g samples of Hg-wool (air-dry weight) were shaken 15 min at 21°C with 25-ml portions of test solution. The mercury content of the liquid was then found as described. Mercury remaining on the wool was found after hydrolyzing a weighed sample in a measured volume of 6*N* HCl under reflux for 22 hr by analyzing the resulting solution. To determine possible loss of mercury during hydrolysis, 6*N* HCl containing 108 mg of mercury per ml was boiled under similar conditions. Recovery was 98.3%.

The following reagents were tested, as 0.01*M* aqueous solutions adjusted to pH 6, for their ability to remove mercury from Hg-wool B: mercaptoacetic acid, mercaptoethanol, dithiothreitol, dithioglycerol (dimercaprol, BAL), 2-mercaptopropylglycine, ethylenediaminetetraacetic acid (EDTA), and citric acid. Attempts to recover as much mercury as possible from Hg-wool B were made by repeated extractions with 0.01*M* EDTA and with 0.1*M* citrate, both at pH 6. An unsuccessful attempt was made to extract mercury from dry Hg-wool B by means of diphenylthiocarbazone in chloroform.

pH Control

To survey effects of pH on adsorption and desorption, we used the universal buffer mixture of Teorell and Stenhagen (1938) at pH's from 2 to 11. This buffer contains 0.01*M* phosphate, 0.0114*M* borate, 0.0067*M* sodium, and from 0.004 to 0.073*M* chloride, depending on the pH.

RESULTS AND DISCUSSION

Sorption by Various Agricultural Products

To test the possible value of wool as an adsorbent compared with other agricultural products, the mercury uptake from aqueous $HgCl_2$ at pH 2 and CH_3HgCl at pH 10 was surveyed for various materials; Table II shows the results. Cotton, rice hulls and straw, and starch bind practically no mercury. Uptake by other materials is roughly proportional to protein content. Wool, feathers, and serum albumin (in solution in a dialyzing bag) are particularly effective. These results support the idea that wool and related materials may be especially useful adsorbents.

Effects of pH

The pH's and times used in the preceding survey were chosen on the basis of preliminary tests with wool. Figure 1 shows the relative binding of mercuric chloride and methylmercuric chloride at various pH's in the Teorell-Stenhagen[12] universal buffer. Table III gives also the binding in moles per gram of wool and the residual concentrations. Under the test conditions, mercuric chloride is taken up in substantial amounts at all pH's from 2 to 10, and best near or below 2 and near 9. Methylmercuric chloride is less adsorbed, and its pH dependence differs; its maximum binding is near pH 10.

Webb[13] has reviewed factors governing interaction of mercury with proteins because of its wide use in studying enzyme reactivity. Mercuric ion has a strong, well-defined tendency to form complexes with chloride and especially hydroxyl ions. Hydroxyl complexes tend to precipitate well on the acid side of neutrality, especially if the salt is well dissociated. Consequently, most sorption measurements have been made in acid media.

TABLE II
Mercury Sorption by Agricultural Products[a]

Material	Sorption from $HgCl_2$ at pH 2		Sorption from CH_3HgCl at pH 10	
	Mercury adsorbed, mg/g	Residual concentration, micrograms Hg/ml	Mercury adsorbed, mg/g	Residual concentration, micrograms Hg/ml
None		600		540
Wheat flour				
whole	4.4	560	5	495
bran	3.3	570		
Wheat gluten	8.9	520	15.6	400
Gelatin	8.9	520		
Silk	8.9	520	13.3	420
Soy flour	11.1	500		
Chicken feathers				
whole	24.4	380	16.7	390
ball-milled	33.3	300	15.6	400
Blood meal	20.6	415	22.2	340
Albumin				
bovine serum	33.3	300		
Wool				
intact	35.6	280	17.8	380
reduced	65.6	10	56.9	28

[a] In these tests, 1.5-g samples were shaken at 21°C for 30 min in 150 ml of solution containing 600 or 540 micrograms of mercury per ml. Binding is calculated assuming all materials to have 11% moisture as found for wool. Essentially no mercury was taken up by cotton, starch, rice hulls, or rice straw.

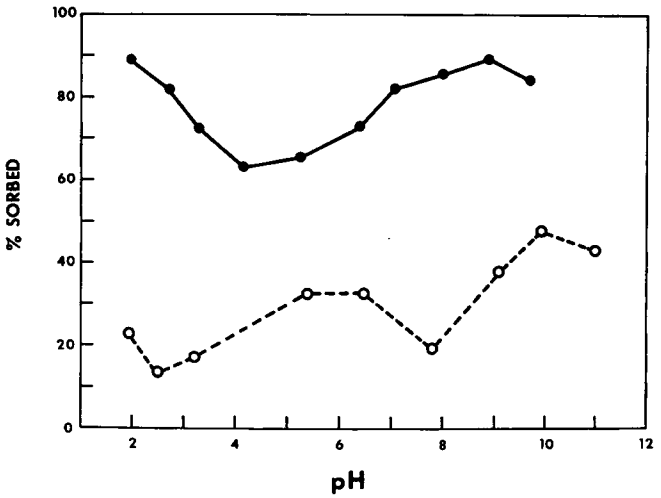

Fig. 1. Effect of pH on sorption of mercuric chloride (upper plot) and methylmercuric chloride by wool (lower plot).

Mercuric nitrate in strong acid and in the absence of complex-forming species gives the divalent cation as the main form of mercury. Mercuric chloride is very little dissociated. In the presence of excess chloride, the anions $HgCl_3^-$ and $HgCl_4^{2-}$ form successively. In 0.1*M* chloride at low pH, about 40% of the mercury is present as $HgCl_2$ (unionized), 25% as $HgCl_3^-$, and 35% as $HgCl_4^{2-}$. Methylmercuric ion forms analogous complexes, but the pK's for dissociation are roughly 1 unit less than for the Hg^{2+} complexes.

In the absence of strongly bound ions other than hydrogen, wool has a region of very little net charge between about pH 5 and 9. This range is smaller in the presence of excess neutral salt. Below this range, wool

TABLE III
Effect of pH on Sorption of Mercuric Chloride and Methylmercuric Chloride by Wool[a]

Mercuric chloride			Methylmercuric chloride		
pH	Sorption, micromoles Hg/g wool	Residual concentration, micromoles/l.	pH	Sorption, micromoles Hg/g wool	Residual concentration, micromoles/l.
1.95	93.6 (88.4%)	0.110	1.95	36.0 (22.8%)	1.097
2.7	86.4 (82.1%)	0.169	2.5	19.4 (13.2%)	1.147
3.3	76.4 (72.6%)	0.259	3.2	30.5 (17.2%)	1.321
4.15	66.5 (63.2%)	0.349	5.4	50.9 (32.6%)	0.947
5.25	69.2 (65.8%)	0.324	6.5	47.1 (32.7%)	0.872
6.4	77.0 (73.2%)	0.254	7.8	27.7 (22.2%)	0.872
7.05	86.4 (82.1%)	0.169	9.1	50.9 (38.0%)	0.748
8.0	90.3 (85.8%)	0.135	9.95	63.7 (47.9%)	0.623
8.9	94.2 (89.5%)	0.100	11.0	49.9 (42.9%)	0.598
9.7	88.6 (84.2%)	0.150			

[a] For each measurement, 1.35 g (dry weight) of wool was shaken at room temperature (21°C) in 150 ml of buffer for 2 hr (mercuric chloride) or for 30 min (methylmercuric chloride). The initial concentration of the mercuric chloride was 190 micrograms Hg/ml; initial concentrations of the methylmercuric chloride varied from 210 to 320 micrograms Hg/ml. The buffer was that described by Teorell and Stenhagen.[12]

assumes an increasing net positive charge as carboxyl groups bind hydrogen. Above this range, imidazole, sulfhydryl, phenol, amine, and guanidine groups successively release hydrogen so that wool is increasingly negative. At pH 1, the cation-binding capacity of wool is near 0.8 equivalent per kilogram; at pH 2, it is 0.6 equivalent at low ionic strength and 0.7 equivalent in 0.1*M* KCl. The net charge on wool will be specifically affected by selective uptake of other ions, such as those containing mercury, and depending on whether a species such as $HgCl_4^{2-}$ loses chloride as it is bound. One of the factors affecting sorption is the relationship of the charges on the wool and on the mercurial. This effect will be diminished by the presence of excess salt, that is, high ionic strength.

Rates of Sorption

Speakman and Coke[2] considered the binding of mercury from $HgCl_2$ in 0.1*N* HCl to have at least two stages. They judged the first step complete in two days at 25°C; binding continued at a much slower, uniform rate for at least 18 days afterward. They found that 2 moles of mercury per kg wool were adsorbed from mercuric acetate in 0.1*N* acetic acid in two days at 25°C. Under the same conditions, Barr and Speakman[3] found about half this amount bound in 1 hr.

Leach[10] judged that an apparently final uptake from $HgCl_2$ in HCl at pH 1 was attained within a day, but noticed that the amount bound varied with the excess in solution. He found much more bound from acetate buffer at pH 6, but in this case a limit was reached only after several days. Excess chloride depressed the binding to about the amount at pH 1. Binding from Tris buffer at pH 9 was intermediate, but a limiting value was not found within 200 hr. At this pH, excess chloride depressed the initial binding rate, but eventually increased the amount bound.

Leach found that methylmercuric chloride was bound slowly and only to a small extent from HCl at pH 1.

Our initial observations suggested that 90% or more of sorption from $HgCl_2$ (in HCl at pH 2) or from methylmercuric chloride at pH 6 might be reached in 30 to 60 min, but that sorption from $Hg(NO_3)_2$ (in HNO_3 at pH 2) was much slower. Results showing rates of binding for these salts are given in Table IV. At the higher concentrations, binding from $HgCl_2$ may reach essentially its equilibrium value in 6 hr, from $Hg(NO_3)_2$ not before one or two weeks. At the low concentration, the rates and amounts of binding from these two salts are much more alike: about 90% of the available mercury was taken up in 1 hr or less. However, these measurements do not define the residual concentration in equilibrium as clearly as desirable for theoretical analysis. Adsorption from methylmercuric chloride appears clearly not to have reached a limiting value, which may be 10% or 20% higher than the highest value cited.

If the uptake is graphed against the square root of the time as in Figure 2, the initial rise will be linear as long as the uptake is limited by the rate of diffusion into and through the wool. The slope is proportional to the diffusion coefficient. As saturation is approached, the graph departs from linearity and approaches a limiting value (ideally). This limit is determined in part by the residual concentration of mercury in solution. As the concentration is increased, the amount of mercury bound per gram of wool increases, but the proportion of the total mercury that is bound decreases. In the results of Speakman and Coke[2] given for comparison, less than one tenth of the available mercury was bound, but initial binding was complete actually before their first measurements at 24 hr. The graph shows the much slower continued reaction already mentioned which has been ascribed to possible reaction with disulfide bonds[10,14] known to occur at higher temperatures.[2]

TABLE IV
Rates of Uptake of Mercury from Various Salts

Time, hr	$Hg(NO_3)_2$, pH 2		$Hg(NO_3)_2$, pH 2		$HgCl_2$, pH 2		$HgCl_2$, pH 2		$HgCl_2$, 0.1*N* HCl[a]		CH_3HgCl, pH 6	
	Residual conc., moles/l.	Sorption, moles/kg	Residual conc., moles/l.	Sorption, moles/kg	Residual conc., moles/l.	Sorption, moles/kg	Residual conc., moles/l.	Sorption, moles/kg	Residual conc., moles/l.	Sorption, moles/kg	Residual conc., moles/l.	Sorption, moles/kg
0	10.4×10^{-3}	0	100×10^{-6}	0	9.9×10^{-3}	0	88×10^{-6}	0	0.200	0	1.58×10^{-3}	0
0.05	—	—	55×10^{-6}	0.0051	—	—	—	—	—	—	1.25×10^{-3}	0.036
0.083	—	—	38×10^{-6}	0.0069	7.6×10^{-3}	0.25	43×10^{-6}	0.0050	—	—	1.18×10^{-3}	0.044
0.167	—	—	—	—	6.7×10^{-3}	0.36	35×10^{-6}	0.0058	—	—	1.13×10^{-3}	0.050
0.25	—	—	25×10^{-6}	0.0083	6.1×10^{-3}	0.42	28×10^{-6}	0.0067	—	—	1.10×10^{-3}	0.053
0.5	10.0×10^{-3}	0.038	10×10^{-6}	0.0100	5.5×10^{-3}	0.48	16×10^{-6}	0.0079	—	—	1.08×10^{-3}	0.056
1	—	—	2.5×10^{-6}	0.0108	—	—	—	—	—	—	—	—
1.017	—	—	—	—	5.5×10^{-3}	0.48	—	—	—	—	—	—
1.033	—	—	—	—	—	—	13×10^{-6}	0.0083	—	—	—	—
1.167	—	—	—	—	—	—	—	—	—	—	1.05	0.058
6	9.75×10^{-3}	0.069	—	—	5.4×10^{-3}	0.50	—	—	—	—	—	—
7	—	—	—	—	—	—	2.5×10^{-6}	0.0094	—	—	—	—
14	—	—	—	—	—	—	—	—	0.1833	1.68	—	—
17	9.5×10^{-3}	0.094	—	—	—	—	—	—	—	—	—	—
24	9.2×10^{-3}	0.136	—	—	—	—	—	—	0.18325	1.70	—	—
30	8.95×10^{-3}	0.158	—	—	—	—	—	—	—	—	—	—
48	8.65×10^{-3}	0.191	—	—	—	—	—	—	0.1829	1.73	—	—
76	8.35×10^{-3}	0.225	—	—	—	—	—	—	—	—	—	—
144	—	—	—	—	—	—	—	—	0.1824	1.78	—	—
360	7.4×10^{-3}	0.327	—	—	—	—	—	—	—	—	—	—
480	—	—	—	—	—	—	—	—	0.1805	1.97	—	—

[a] Data of Speakman and Coke.[2]

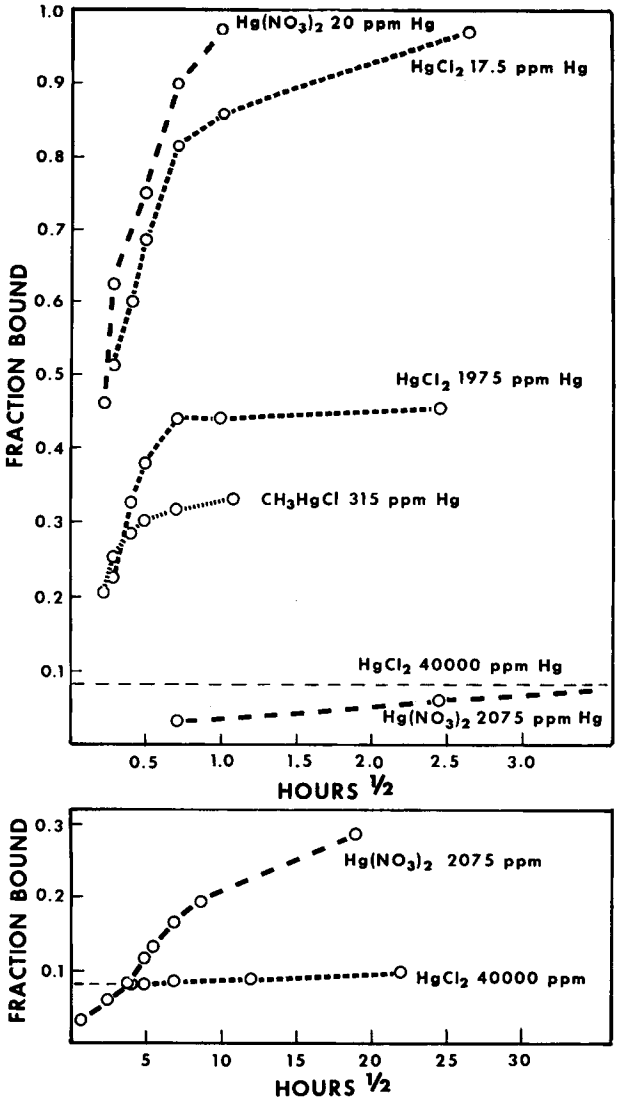

Fig. 2. Rates of uptake of mercury by wool from various salts. Data for $HgCl_2$ at the highest concentration are from Speakman and Coke[2].

Effects of Concentration

Table V compares published adsorption results with ours, which we have carried to lower concentrations. The main point of practical interest is that as the concentration is decreased, sorption of inorganic mercury, either the chloride or the nitrate, from acid solution becomes very efficient. In the parts-per-million range, the partition coefficient reaches values of several thousand, and then increases in the parts-per-billion range. It is this

TABLE V. Sorption of Mercury Salts by Wool

Residual concentration, C, moles/l.	Sorption x, moles/kg	Partition coefficient x/C	Residual concentration C, moles/l.	Sorption x, moles/kg	Partition coefficient x/C
Mercuric acetate in 0.1*M* acetic acid, 48 hr, 25°C (Speakman & Coke[2])			1 hr, 25°C (Barr & Speakman[3])		
0.034	1.58	46	0.0123	0.47	38
0.081	1.93	24	0.0756	1.11	15
0.180	1.97	11	—	—	—
Mercuric chloride in 0.1*M* HCl, 25°C, mostly about 2 days (Speakman and Coke[2])					
0.0055	0.46	84	0.089	1.12	13
0.014	0.59	42	0.135	1.47	11
0.023	0.66	29	0.183	1.76	10
0.042	0.79	19	—	—	—
Mercuric chloride in 0.2*M* HCl, 20°C, constant, 1 to 8 days (Leach[10])					
0.0001 (0.000145)	0.08	800 (550)	Figures in parentheses result from making an arbitrary		
0.000325 (0.000345)	0.14	430 (410)	correction in the wool weight for possible sorbed water.		
Mercuric chloride in HCl, pH 2, 21°C, 2 days (our results)					
2.5×10^{-6}	0.00944	3800 (7 hr)	0.00014	0.10	780
5×10^{-6}	0.01	2000	0.00060	0.25	430
"	0.02	4000	0.00499	0.47	93
"	0.03	6000	0.00538 (6 hr)	0.50	93
Mercuric chloride in HCl, pH 2, room temperature, 15 min					
2×10^{-8}	0.000003	170	Analyses in p.p.b. range by courtesy of Dean Yeaman,		
2.7×10^{-7}	0.00003	90	Richard Gregory, and John Shakley, Dow Chemical		
5×10^{-8}	0.0005	10,000	Company, Pittsburg, California		
Mercuric nitrate in 0.5*M* KNO_3, room temperature, 4 days (Hojo[4])					
0.018	0.62	34			
Mercuric nitrate, pH 2, 48 hr (our results)					
2.5×10^{-6}	0.01	4000 (1 hr)	0.00125	0.23	180
5×10^{-6}	0.01	2000	0.00728	0.33	46
"	0.03	7000	0.00743 (15 days)	0.33	44
0.000017	0.13	7000			
Methylmercuric chloride, pH 1, 20°C, 170 hr (Leach[10])					
0.00044	0.013	30			
Methylmercuric chloride, pH 6, 21°C, 30 min (our results)					
0.00001	0.007	700	0.00015	0.028	180
0.00002	0.012	600	0.00100	0.050	50
0.00005	0.023	450	0.00105 (70 min)	0.058	56

property as much as any other that leads us to suggest that wool may be a practical adsorbent for mercury.

Sorption of methylmercuric chloride appears less favorable. At pH 6, its partition coefficient is about one tenth of that of the inorganic mercury compounds at low pH, and the amount bound is also less by a factor of about 10. However, useful binding is rapidly achieved, and the amounts that can be bound may be higher by 20% than those observed after 30 min.

Binding Mechanisms

Detailed interpretation of the binding processes and stoichiometry presents a substantial challenge. If the mercury-containing units were taken up independently on a single type of binding site in such a way that adsorption of the first unit did not affect adsorption of the next, adsorption would follow a Langmuir isotherm. In this case, as Scatchard[15] shows, a straight line would result if x/C is plotted against x, where x (for this discussion) is the gram atoms of mercury taken up per kilogram of adsorbent (or millimoles per gram) and C is the residual concentration in moles per liter. The intercept of such a line on the x-axis indicates the concentration of binding sites. The intercept on the x/C axis defines the classical first association constant. This can be regarded as a limiting partition coefficient.

However, when the sorption data for wool are graphed according to Scatchard, the resulting Figure 3 shows *curved* isotherms without plausible intercepts. This curvature may result from the existence of two or more types of binding sites, which may react at different rates with mercuric chloride.

Scatchard shows that the curvature in the case of proton binding to proteins can be very nearly accounted for by allowing for the changing electrostatic interaction between the protein and the species being bound as successive units are bound. We have tried unsuccessfully to find an empirical, exponential correcting factor that will make the graph for $HgCl_2$ linear. The observed x/C shows no indication of approaching zero at high uptake. This circumstance suggests that part of the mercury may perhaps be taken up by preferential solubility without localized binding and described by Raoult's law.

When the sorption results are graphed logarithmically (Fig. 4), they are seen to be roughly represented by isotherms according to Freundlich. For the inorganic salts in acid media (pH 2–4),

$$\log_{10}x \cong 0.33 \log_{10}C + 1.9_4. \quad (1)$$

This gives the mercury sorption x (milligram of Hg bound per gram of wool) for a given residual concentration C (gram of Hg per liter), usually within a factor of 2 within the range of C from 0.001 to 40. We confirm that wool can bind more than half of its weight of mercury from concentrated mercuric acetate or mercuric chloride.

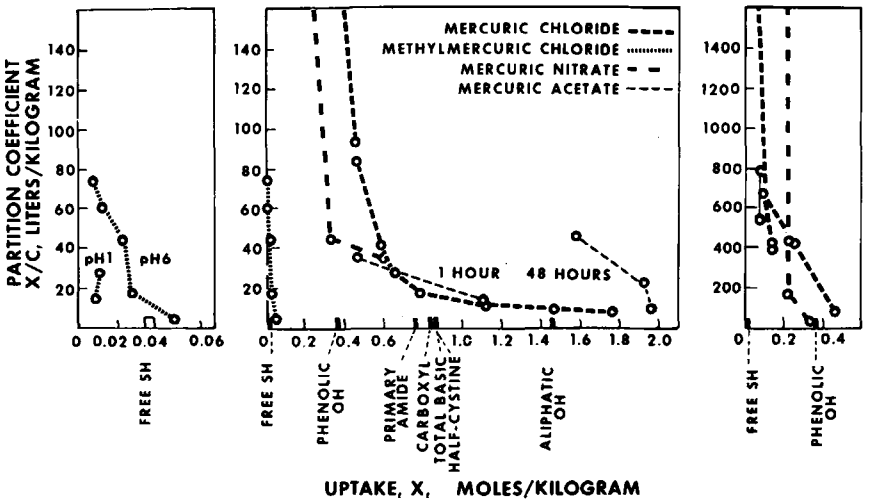

Fig. 3. Sorption of mercury by wool from various salts at various concentrations, Scatchard[15] plot. Contents of the various reactive groups in wool are indicated. Not all of these bind mercury. Data for methylmercuric chloride at pH 1 are from Leach[10] and show the slow uptake from 72 to 170 hr at 20°C. When the lines extend to the top of the graph, they are placed to show the position of additional points beyond the range of the graph. The highest binding shown for mercuric nitrate (center and right graphs) is taken from Hojo.[4] Results for mercuric acetate with 1-hr contact are from Barr and Speakman[3]; with 48-hr contact, from Speakman and Coke.[2] For mercuric chloride, results from Speakman and Coke[2] are shown as the range with highest binding in the center graph, together with one of our data, which are shown and indicated in the right-hand part. Two sets of paired points (at 0.08 and 0.14 moles/kg) are data from Leach[10]; the spread shows our uncertainty about the basis for calculation.

For methylmercuric chloride at pH 6, the corresponding Freundlich relationship is

$$\log_{10} x \cong 0.4 \log_{10} C + 1.3_0. \qquad (2)$$

This holds with about the same precision as above in the range of C from 0.001 to 0.2 g Hg per liter. In this range, the binding varies from one seventh to one fifth that from $HgCl_2$.

The Freundlich relationship (extrapolated) can be used to make a rough estimate of the amount of wool needed to remove mercury from water under given conditions. For instance, to remove 138 mg Hg from a liter of industrial effluent to bring it to the mandatory maximum level of 5 micrograms per liter, permitted in a public water supply, would require about 0.1 kg wool at pH 2.

The vertical dashed arrow at 0.1 ppb, a representative value for mercury in sea water, indicates the accumulation of mercury in the animal part of the sea food chain; X indicates roughly the concentration in plankton animals; and the head of the arrow indicates the content expected in large predatory fish. The latter content is a few times higher than the tentative allowable maximum in individual foods. Note that the concentrations in

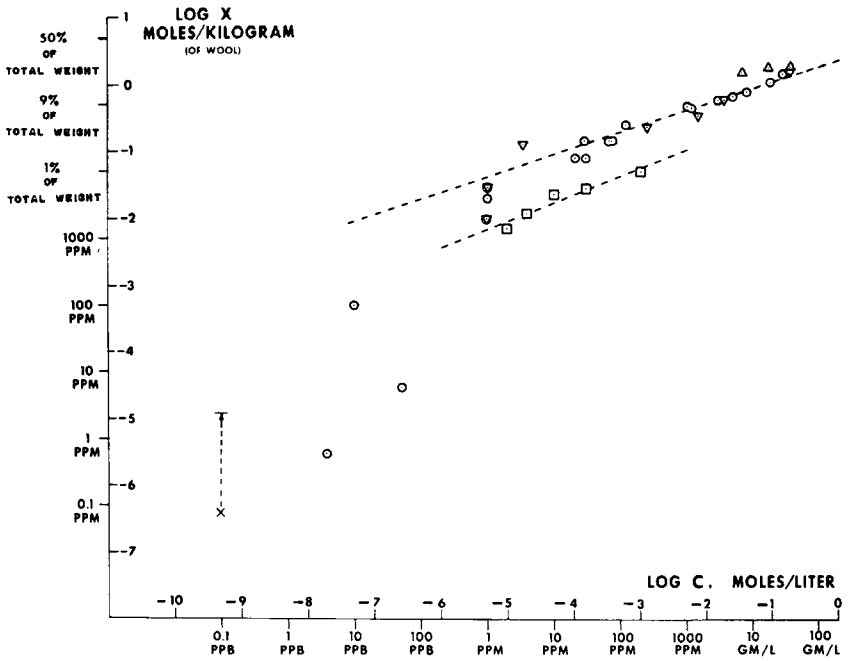

Fig. 4. Sorption of inorganic salts and methylmercuric chloride to wool: (⊙) mercuric chloride; (▽) mercuric nitrate; (△) mercuric acetate (these in acid media with the corresponding anions); (⊡) methylmercuric chloride pH 6. The vertical dashed arrow indicates the accumulation of mercury in the animal part of the sea food chain.

fish are less than would be expected for wool in equilibrium with sea water as indicated by the Freundlich lines. However, the difference is roughly consistent with the actual protein content of fish. The idea that the mercury content of fish protein approximates the value expected from sorption equilibrium needs to be evaluated critically in comparison with evidence for food chain accumulation.

Recovering of Bound Mercury from Wool

The pH dependence of binding shown in Figure 1 suggests that a slightly acid pH, 4, would be best for removing inorganic mercuric ion from wool, and a lower pH, 2.5, for the methylmercuric ion. Actual trial in 0.01*M* phosphate suggests that pH 6 is most favorable for desorbing inorganic mercury. We then attempted to increase the amount desorbed at pH 6 by using various complexing agents as 0.01*M* solutions. The most useful reagents appear to be aqueous ethylenediaminetetracetate (EDTA) and citrate. More than 90% of the mercury is recovered in concentrated form from the wool. The amount of mercury remaining with the wool in each case is roughly in the proportion of one mercury atom to two sulfhydryl groups.

Of the large amount of mercury taken up by reduced wool from $HgCl_2$, only 17% could be extracted by EDTA. The remainder from either $HgCl_2$ or CH_3HgCl indicates a possible content of 0.3 to 0.4 mole/kg of available sulfhydryl sulfur in the reduced wool (as 1 SH:1 Hg). Regardless of the mechanism by which the mercury is originally adsorbed, it seems likely to move to sulfhydryl groups, to the extent that these exist, when circumstances are favorable (given time enough and a high enough pH).

The very small dissociation of mercury mercaptides may make it hard to discover an effective soluble complexing reagent that can successfully compete with sulfhydryl groups in proteins, especially if the mercury is bound in proteins by multiple interaction. The very slow excretion of mercury after it has become established in the human body suggests that comparable firm binding has occurred. (In this case, the rate of excretion may be a measure of the catabolism of the proteins to which mercury is bound.) Thus, studies of desorption from wool may be useful in medicine.

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