HUMAN FOOT PERSPIRATION, ITS NATURE AND INTERACTIONS WITH FOOTWEAR

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I. Introduction

Investigations on perspiration, particularly in regard to feet, are not easy to carry out; observations have to be made under a variety of conditions and complicating factors. A man's foot perspiration may be alkaline whilst another's is acid, and the same person may show different reactions on the same day.

Such variations are reflected in a crude way by people wearing the same make or brand of footwear—no matter how good in quality the latter may be, a white deposit occurs on some pairs, cracks in the leather vamps of others or unsightly stains on willow calf or other coloured types.

The information available in the literature on perspiration generally is incomplete and scattered. Sweat is described (Bainbridge and Menzies, 1919) as a clear colourless fluid containing 99 per cent. water, sodium chloride is the predominant solid dissolved in it with traces of protein, fatty acids and urea. The secretion from the sebaceous glands known as sebum coexists with sweat to protect the skin and impart suppleness. It is an uncertain form of fatty acid—albumin compound with cholesterol. Sulphates and phosphates are also found in the sweat and desquamated cells in the sebum (Wilson, 1923). Freshly secreted, sebum is an oily mass (Abderhalden, 1908) which on air exposure solidifies to a greasy mixture on the skin surface. An analogous phenomenon occurs when kidney function is impaired and causes an accumulation of urea in the blood (Matthew, 1916). This results subsequently in the actual crystallisation of urea on the skin when the perspiration evaporates away. Cameron (Hammarten, 1911) reports certain samples of filtered human perspiration to be alkaline and others acid. In gout, diabetes and cystinuria, perspiration has been observed to furnish respectively uric acid, sugar and cystine. Bile colouring matter has not yet been reported with any degree of certainty in diabetes, but coloured perspiration (chromhidrosis) has actually been noted as a true blood sweat.

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Skatoxyl, sometimes indoxyl, aromatic oxyacids, alkyl phenol sulphonates and creatinine, as addition products have been detected so far only in animal perspiration.

Such findings in the literature as the above instances were based on different parts of the body, *e.g.* the cheek or armpit. Furthermore, some of the experiments involved artificial stimulation, *e.g.* Argutinsky collected a half-pint of perspiration this way during three-quarters of an hour in a steam bath experiment in order to find urea. In a similar manner, Cramer reports ammonia in addition.

The present paper is a study of perspiration as confined to the human foot in the absence of artificial stimulation. It seeks anew from actual experience what can be found in the nature of perspiration, the amount of moisture not being regarded as very important nor the percentage of dissolved solid matter. The important object rather is the solute that cumulatively collects in the proximate vicinity of the foot, and, in studying its nature, its behaviour in contact with footwear materials is doubtless of hygienic significance.

II. Methods of investigation

Several volunteers of both sexes and all enjoying normal health wore chemically purified hose during dry warm weather.

The hose (light grey, white or cream) were of cotton or wool or a mixture of both, and were repeatedly boiled in strong alcohol till no more than 0·05 g.[1] solute impurity was obtained from each half-pair. They were next repeatedly exhausted with hot distilled water until free from chlorides and sulphates and again no more than 0·05 g. solid impurity was obtainable from each half-pair. After air drying overnight, the hose were subjected to a period of 7 days' *actual* wear.

The deposit which accumulated during this period upon the hose consisted of the solutes from perspiration itself, together with extraneous matter, partly derived from the shoes. The following plan was adopted:

The hose were soaked overnight in lukewarm alcohol, then the light brown alcoholic extract was filtered, concentrated at less than 45° C. *in vacuo* and finally evaporated down on a tared shallow basin at low temperature. The extraction was then repeated just boiling with fresh alcohol and the solvent again recovered.

The residual hose were then extracted at 40–45° C. with sufficient distilled water to cover them, and the aqueous extract filtered. Three further extractions with distilled water were performed in a vigorously boiling water-bath and finally filtered.

(*a*) The dried alcoholic extract

This was invariably dark brown; it was treated with a little warm water and filtered. The residue was tested for cholesterol, fats, phospholipins and fatty acids; the aqueous filtrate after charcoal treatment was tested for

[1] g. denoting grammes throughout this paper.

urea, lactic, hydroxy and fatty acids, reducing sugars, cane sugar and soap.

Lactic acid and urea were specially looked for by Hopkins and the specific urease tests respectively; in the latter case, the fatty acid content was first titrated to a blue end-point with bromothymol-blue as indicator prior to the soya bean application.

(*b*) THE AQUEOUS EXTRACTS

These were tested for *p*H, solubles, starch, urates, chlorides, sulphates, ammonium salts, urease and lipase (on olive oil and boiled milk substrates) for low temperature extracts only, proteins, especially gelatine, albumoses and peptones, glycogen, dextrin and earthy phosphates.

In testing for proteins various precipitants were used including Esbach's, Brücke's and Almen's solutions, also sulphosalicylic acid and ammonium sulphate; in addition xanthoproteic, Millon's, Molisch's, glyoxylic, biuret and sulphur colour reactions were applied.

In regard to enzymes, it was first proved by a control test that the prior process of boiling alcoholic extraction did not kill the enzymes sufficiently to invalidate the low temperature aqueous extraction. Where contamination by tannin was found, the urease test was applied after detannisation and elimination of introduced lead.

Table I contains results based on a select few and shows only those substances which were actually found.

Table I

Item estimated (g.)	A Young girl	B Female Adult	C Male Adult	D Male Adult	E Male Adult	F Young Boy
Total dried alcoholic extract	1·158	0·281	0·703	0·750	0·539	1·318
Cholesterol crystallised	0·053	0·090	0·130	0·174	+	0·121
Phospholipin	+	–	+	–	–	+
Fatty acid titration value *N*/10 c.c.	14·0	+	11·7	11·0 (not sharp)	5·6	14·0 (not sharp)
Urea	–	+	–	–	+	–
Tannin (*ex* shoe)	–	–	–	+	–	+
Low temperature aqueous extract						
*p*H	7·0	6·6	5·2	5·6	6·2	
Water solubles	0·581	0·160	0·563	0·560	0·865	0·900
'Cl	0·112	0·010	0·066	0·0435	0·098	0·0525
$''PO_4$ + gelatin	+	+	+	+	+	+
Xanthoproteic, Millon's and biuret	+	+	+	+	+	+
Tannin (*ex* shoe)	–	–	–	+	–	+
$''SO_4$	0·036	0·016	0·0425	0·146	0·069	0·091
1st high temperature extract						
*p*H		6·2		5·2	6·2	
Water solubles	0·294	0·046	0·392	0·364	0·247	
'Cl	0·027	0·0035	0·020	0·014	0·009	
$''SO_4$	0·0295	0·0060	0·032	0·059	0·022	
2nd high temperature extract	0·189	0·024	0·285	0·126	0·170	
Total aqueous extracts isolated	1·199	0·246	1·4065	1·163	1·423	0·900

The table shows positive but not marked indication with xanthoproteic and Millon's colour reactions; keratin was present in all cases derived, like gelatin, from the breakdown of epithelial cells shed from the heel.

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III. Synthetic foot perspiration

Consideration of the quantities of the constituents in Table I leads to the following preparation as an approximate general representative character.

White cholesterol crystals (from ox or sheep brains)	1 g.
Urea crystals	0·05 g.
Lactic acid B.P.	5 drops
Butyric acid, commercial	5 „
Saturated alcoholic egg lecithin as phospholipin	10 „
Melted Russian tallow	1 drop
Saturated aqueous potassium sulphate	1 „
10 per cent. aqueous sodium phosphate	1 „
Normal sodium chloride solution	5 c.c.

The cholesterol and urea were rubbed down in a shallow dish with the fatty acids, the commercial quality of butyric acid being used in order to include small amounts of valerianic and capric acids. On warming to 40° C., the mixture set into a thick white homogeneous paste probably denoting some chemical change. Next, the phospholipin and the remaining ingredients were stirred intimately into the paste. All the constituents should be reasonably free from iron.

Properties of synthetic normal perspiration

Such a preparation is of interest. Due to oxidation of the cholesterol and phospholipin, it acquires, like the naturally excreted perspiration, a yellowish tinge on air-exposure and a dirty brown with age.

It also reacts acid to thymol blue or xylenol blue paper (pH 2·4–2·7), the same as that of the aqueous filtrate from the dried alcoholic extract of the worn hose.

Such acidity may be expected if we merely consider the fatty-acid titration values alone. Taking an average value as 10 c.c. $N/10$, we may imagine that at one phase during wear as much as possible of the moisture has been evaporated from the hose under the influence of heat, porosity and thermal conductivity of shoe materials, flexure, etc. Then, although some acids are volatile, we should have temporarily an acidity due to fatty acid of about normal strength. The pH values of acetic, butyric and lactic acids of this strength are respectively 2·43, 2·40 and 1·96—all well within the working range of the indicator test.

Any possible injurious action of such acidity is, however, open to question, owing to the basic counteraction of the cells shed during the reproductive process in the epithelium. The basic character of these cells is certainly evident from the gelatine detected in the aqueous extracts of the hose.

An important property of foot perspiration is its power, through its hydroxy-acid content of gradually detannising full chromed uppers. Thus if pelt (collagen) is well treated with a basic chromium tanning agent, a square inch piece of the resulting leather will barely shrink when immersed in boiling water; yet if previously acted upon by perspiration for a sufficient length of time, say one to two months, the shrinkage may be considerable in the boiling test.

Such detannisation may be observed as a common occurrence on most

people's shoes as crackiness on the leather vamps, in or amongst the creases caused by flexure, especially around the inside ball of the foot.

Other effects observed on footwear, such as unsightly stains, white deposits on the foreparts, and stiffened or hard shiny areas near the toes, have been traced to normal perspiration functioning chiefly as solvent water. As a solvent, perspiration washes out dextrin or salts from the cotton fabric linings in the interior of the shoe, and works them through the leather vamps in the act of walking. The moisture then evaporates from the surface pores outside, leaving salts or dextrin stains in the grain layer of the leather.

IV. ABNORMAL FOOT PERSPIRATION

Formidable as such effects can be, they are worse when caused by subjects in abnormal health. They form the experimental basis upon which an insight has been gained into the character of abnormal foot perspiration. Incidentally, this point illustrates the difficulty encountered in making an exact investigation in a reasonable time, for the pathological element as a complicating factor is present in probably 70 per cent. of the population. Thus the presence of weak ankle or what is popularly known as "tired or aching feet" is attended by abnormal changes in the composition of sweat or any form of foot secretion. Lactic acid or urea in enhanced proportion is probably the most frequent result from "tired feet".

The following types of abnormal foot perspiration have been met: (*a*) glucose, (*b*) blood, (*c*) uric acid.

(*a*) *The glucose type*

It was ascertained that the wearer was definitely diabetic; in fact, when neither the fabric linings nor the leather materials contained any glucose, the abundant white deposit diffused all over the shoe uppers was the first intimation that the wearer himself was the source.

(*b*) *The blood type*

In this case there was difficulty in tracing whether true blood sweat occurred or mere abrasion only was present. The wearer wore patent leather shoes which had become quite stiffened by the blood exudation. A mere ammoniacal swab of their surface showed a positive benzidine test; moreover, the red powder deposited on the fabric lining could be still dissolved in cold water and coagulated by boiling. If chromhidrosis is usually accompanied by a foetid odour, this was not observed, but the author believes that the foetid state is probably caused by unknown enzymes and living organisms not yet isolated.

(*c*) *The uric acid type*

This is by far the most frequent type. Urea, uric acid or urinary matter is found lodged within the pores of the leather substance and the general appearance of the affected leather, particularly near the toes and arched region,

is characteristic—broken grain, soft and detachable, alike for calf and glacé kid. Even the hard enamelled surface of patent leather is rendered soft, almost greasy. A square inch of such affected leather has been known to furnish enough voluminous grey uric acid crystals to fill a small ignition tube.

The identification of uric acid itself from the leather is not served very well by the murexide reaction. The best method involves the use of Folin's phosphotungstate reagent on the hot aqueous extract of the leather, as evaporated down in the usual way with a crystal of oxalic acid; prior to the actual positive indication of a deep blue, due precautions are, of course, taken to eliminate any phenolic groups by thorough alcoholic separation.

In one case this test proved surprisingly negative. A pair of ladies' black glacé kid boots showing the scaly grain had the affected parts of the uppers boiled out in water—a marked urinary odour and deeply coloured muddy extract was obtained. On further investigation, the extract yielded as much as 24 per cent. by weight of the leather as logwood colouring matter, which, like litmus, had probably undergone fermentation with production of the urinary odour. Evidently the kid leather was an exceptional and rare case of poor production and faulty dyeing—the uric matter was not derived from the perspiration.

Of greatest frequency are those cases which analytical studies disclose as containing two or more of the following in the cracky parts of the leather: (i) normal salts in the leather, including sodium sulphate, (ii) acid sodium urate, (iii) acid ammonium urate, (iv) ammonium carbonate, (v) small quantities of bisodium or bi-ammonium urates, (vi) urea.

In most of these cases the possibility of an external cause of uric acid deterioration could not be entertained, and the effects had to be considered as arising from a gouty condition. In this connection, therefore, it is well to bear in mind that the presence of collagen is not a stabilising factor for any urea secreted by perspiration, and in the course of time, micro-organisms such as torulae or the group of bacteria known commonly as vibrios might cause fermentation of urea or urates to ammonium degradation products.

Analytical examination of uric acid types

By the appearance alone, a pair of box calf Eton boots was correctly diagnosed as having undergone uric acid deterioration. During the analysis of the abnormal aqueous extracts the air of the laboratory became decidedly unpleasant and rapid ventilation had to be resorted to; a large part of the uric deposit existed in the uppers as ammonium salt, as ammonia could be directly distilled over without any preliminary Kjeldahl digestion.

Products detected besides ammonium salts were: urea, glucose, uric acid and non-tanning phenolic matter; the last item was probably derived from the vegetable tanned leather lining by the washing movement of perspiration. Their decomposable and variable nature did not permit in the present case of a satisfactory isolation of crystalline uric acid—the final form was solid but sticky as well as amorphous.

Table II gives an idea of the general composition of the upper leather. The outstanding features in the affected parts are the high soluble matter, ash and nitrogenous contents.

Some quantitative details:

(i) Direct distillation of 0·7 g. affected leather yielded 40·1 c.c. $N/10$ actual titre.

Digestion of 0·5 g. yielded 50·8 c.c. $N/10$ (factor 1·024). The true actual titre for collagen is, therefore, 44·32 c.c. $N/10$ per g. material or 35·7 per cent.

Table II

Percentage volume at 75 % R.H.	Relatively unaffected parts (near leg)	Affected parts (vamp and quarters)
Moisture	17·00	13·64
Fat	3·30	3·60
Water solubles	2·12	22·72
Ashed solubles	0·52	4·80
Chromic oxide in the soluble ash	⊱ 0·10	⊱ 0·10
Total ash	6·70	12·60
Total chromic oxide in the ash	4·40	3·13
*(Collagen)	66·00	81·80 (only an apparent value)
†Total of items directly accounted for	94·60	—
Shrinkage	19·10	Considerable

* Every 100 c.c. $N/10$ ammonia from Kjeldahl analysis = 0·786 g. collagen.

† Items unaccounted for merely include acid radicals (sulphate, chloride or fatty acid) from chrome combination.

The total of items directly accounted for in the affected parts thus became 83·46 per cent. It therefore required another 11·14 per cent. to equal, at least, the total for the unaffected parts.

(ii) Digestion of 0·4 g. water-soluble matter yielded 43·2 c.c. $N/10$ actual titre. This required a small correction owing to moisture absorption of the test sample on air-exposure. The factor is 1·136/1·244.

Now the amount of leather as in (i), viz. 0·7 g., contained $0{\cdot}2272 \times 0{\cdot}7$ or 0·159 g. water solubles, so that the titre on the present basis would be only 18·81 c.c. not 40·1 c.c. The difference of 21·29 c.c. titre, therefore, is an equivalent of ammonia released from the chromed fibres by boiling caustic soda.

Bearing these two additional data in mind and the fact that the uric perspiration has caused an increase of over 4·0 per cent. in the ashed water-soluble content, we arrive at the following general composite character of the affected leather:

	Percentage volume at 75 % R.H.	
Moisture	13·64	
Fat	3·60	
Water solubles	6·87	Total 22·14
Urea		
Acid sodium urate	15·27	
Total ash	12·60	
Ashed water solubles	4·80	
Total chromic oxide	3·13	
Collagen	35·70	
Ammonium urate (acid form)	11·52	
Total accounted for	94·4	

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The formation of chrome urate has not been lost sight of, but tests indicate that, if formed, it would be soluble and its presence detected in the soluble ash. The latter, however, only shows a negligible content of chromium.

The above analytical example forms an absolutely consistent whole in accordance with experimental data.

Summarising this section, perspiration in gout causes a partial disruption of the collagen material and the formation of urea and urates.

V. Conclusions

Human foot perspiration is essentially an organic dispersion in salt solution and regarded in this way, as an emulsion, it would include sweat and sebum.

Judging from its effects on footwear, it is fairly active chemically and physically. The physical action would be more noticeable in the case of profuse perspiration from a healthy subject, whilst the chemical character would be evident markedly in abnormal perspiration arising from a pathological case. In an average manner, normal perspiration functions chiefly as an aqueous solvent with hydroxy-acid characteristics of an initially small extent.

It is, however, in the cumulative action of perspiration that the total solids of the emulsion bear some significance. This significance has a twofold aspect:

(i) On the one hand, the clothing of the foot may be of unsuitable material, *e.g.* as an extreme case patent leather for advanced gouty subjects, and

(ii) On the other hand, the solvent or chemical interaction with external agents may aggravate trouble following on mere absorption alone through the skin, *e.g.* aniline or nitrobenzol from wrong shoe dyes has been known frequently, in Holland, France and America, to cause toxic symptoms, through successive solubilisation by perspiration.

Further work is desirable, with the right personnel as experimental subjects, to establish the presence of enzymes. Failure so far to detect them may probably be the result of limitations of method and conditions.

If enzymes or even living organisms may exist in perspiration, added important significance would be cast upon the whole investigation.

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