Kinetics and equilibria of tea infusion. Part 10—The composition and structure of tea scum

Michael Spiro & Deogratius Jaganyi

Department of Chemistry, Imperial College of Science, Technology and Medicine, London UK, SW7 2AY

A simple technique is described for collecting the film of tea scum, which forms on the surface of tea brewed in hard water. Powder diffractometry showed the scum to be amorphous. Scanning electron micrographs revealed the existence on the scum of islands of calcium carbonate which could be removed with dilute hydrochloric acid (the underlying polymeric scum dissolved only in highly concentrated hydroxide solution). Inorganic carbonate was confirmed by solid state ^{13}C-NMR and by FTIR measurements: these techniques also pointed to the presence of hydroxyl groups, carbonyls and some unsaturated organic linkages. Molar masses of the order of 10^3 g were obtained by the MALDI method for both the original and the HCl-treated scums. Chemical micro-analysis showed that the percentage of calcium rose from 3 to 7 wt% as the scum developed. The calcium, as well as smaller amounts of magnesium, manganese and sodium which were present, were all removed by the HCl treatment. The empirical formula of the organic scum matrix contained *c.* 45 carbon atoms.

INTRODUCTION

In hard water areas an unsightly film, called tea scum or tea scale, forms on the surfaces of tea infusions. Little is known about this scum. The only author to have dealt with this topic is Kooijmans (1940), in a 2½ page paper in Flemish later plagiarised in another Dutch journal by van Schaik (1953). Kooijmans wrote that there are two types of scum. The kind which formed a thin layer on the tea was said to be due to the spontaneous extraction of organic tea compounds, but to be independent of the water hardness and to occur even in distilled water. Moreover, this layer grew faster at lower pH, was independent of the presence of oxygen or carbon dioxide, was soluble in ether and strong alkali, and stopped growing when the surface was completely covered. Kooijmans' second type, an enhanced scum, was produced within teapots and mugs. Although it was said to consist of the same material as the thin scum, it did depend on water quality and was initiated by the decomposition at the surface of calcium bicarbonate to form $CaCO_3$. The enhanced scum formation could be stopped by boiling the water, lowering the pH or adding sodium sulphate. However, Kooijmans' paper contained no numerical data on

scum formation and no tables or graphs. In a third Dutch paper, Schurer (1960) mentioned that calcium and magnesium salts in tap water can react with tea components to produce a dull infusion and much scale in the cup and pot and floating on the tea itself. Thorough boiling suppressed the scale. Although later workers (Roberts & Smith, 1963) compared the appearance, composition and pH of tea brewed in distilled water and in hard London mains water, nothing further was said about the presence of scum.

In view of the lack of quantitative knowledge about tea scum, we have undertaken a systematic investigation of its formation and composition. The present paper reports on a simple method of collecting and weighing the scum and on the chemical and physical examination of the material. The factors which influence the extent and rate of scum formation have been studied in a following paper (Spiro & Jaganyi, 1994).

MATERIALS AND METHODS

The hard water used was London mains tap water (whose composition was obtained from Thames Water plc) or synthetic hard water made by dissolving $CaCl_2$ (BDH AnalaR, 2.72 mmol dm^{-3}) and $NaHCO_3$ (BDH AnalaR, 5.44 mmol dm^{-3}) in distilled water. Standard tea brews were prepared by heating 800 ml of this

water in a wide 1 litre glass beaker to 80°C on a hot-plate and then transferring it to a thermostat bath set at 82°C. After the water temperature had reached and stabilised at 80°C, one teabag of a major commercial blended black tea (Typhoo, Premier Brands) was lowered into it and the infusion was stirred in a reproducible manner for 5 min. The teabag was then removed, the surface scum and foam scooped off as described below, and the pH of the infusion was measured. The beaker was then covered with a watch-glass placed concave side down so that the water vapour which condensed on it ran back into the tea solution at the walls of the beaker without significantly disturbing the surface layer of scum. After various periods of standing (often 60 min), the scum was scooped off with a piece of clean aluminium cooking foil which had been cut into the shape of a spade and carefully pressed flat to remove any wrinkles. By careful manipulation, all the surface scum could be collected on the foil. It was then washed off with a jet of distilled water into a sintered-glass filter crucible and sucked dry at a water pump. The crucible and its contents were dried overnight in an air oven set at 80°C, cooled in a desiccator and weighed. The scum from many such experiments was aggregated and crushed to provide enough material for the various kinds of analysis.

In a later set of experiments, scum was collected from numerous tea infusions which had been allowed to stand at 80°C for specific periods of time (15, 60 and 240 min). Half of these samples were then treated for 30 min with 0.1 mol dm^{-3} HCl to dissolve any calcium carbonate and similar material, washed and dried. These 'timed' treated and untreated samples were sent for chemical microanalysis to MEDAC Ltd at Brunel University, while the earlier mixed samples were used for other physicochemical examinations.

RESULTS AND DISCUSSION

Appearance, thermal behaviour and solubility

Tea scum which had been allowed to form for 4 h at 80°C is shown in Fig. 1 after it had been carefully transferred to a beaker of fresh water. The dried material was crumbly and brown in appearance.

On steady heating, the scum treated with hydrochloric acid became black at 214°C. It retained this colour on cooling, indicative of some decomposition to carbon. No such colour change was seen on heating the untreated scum. Neither material had melted, even at 300°C.

The scum dissolved only in highly concentrated sodium hydroxide solution, but was insoluble in a wide range of organic and inorganic solvents (methanol, ethanol, propan-2-ol, 2-methylpropan-2-ol, allyl alcohol, acetone, 1, 4-dioxan, diethyl ether, tert-butyl acetate, chloroform, triethylamine, acetonitrile, toluene, dimethyl methylphosphonate, hydrochloric acid and sulphuric
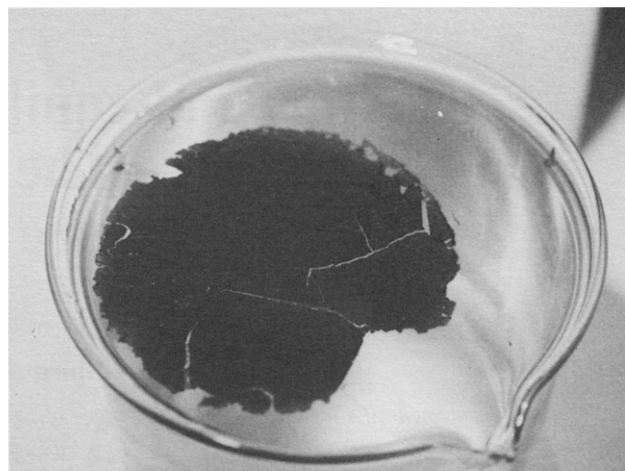

Fig. 1. Top view of 4 h tea scum floating on water.

acid). This made it virtually impossible to carry out standard NMR or mass spectrometric analysis. However, for the purpose of analysing for the presence of metals by inductively coupled plasma, the scum could be oxidatively destroyed by adding concentrated nitric acid, warming the mixture and then adding a small amount of hydrogen peroxide.

Powder diffractometry

When the scum was analysed with a Siemens D-500 powder diffractometer, the plot of intensity versus diffraction angle was a curve with broad bumps but no sharp peaks. The scum was therefore not crystalline. In contrast, a diffractogram of the white precipitate which floated on hard water heated to 80°C consisted of a series of sharp peaks which coincided exactly with the peaks obtained with pure calcium carbonate in the form of calcite.

Scanning electron microscopy

The scum was crushed into powder, attached to aluminium with Araldite glue, coated with gold for structural analysis or with carbon for analysis of the
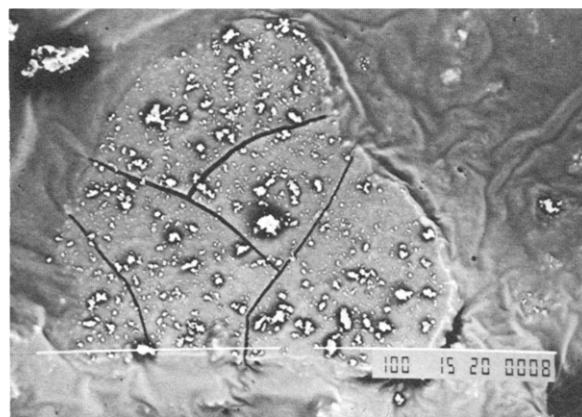

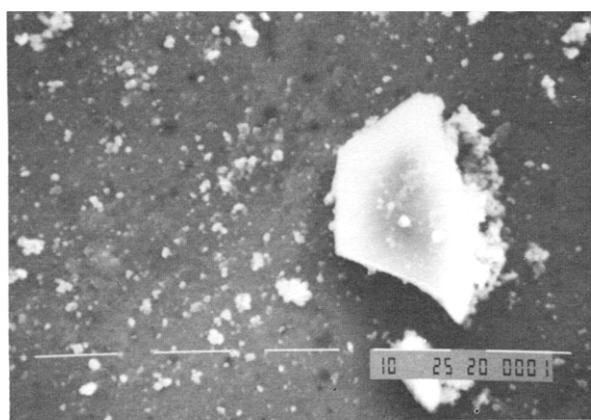Fig. 2. Scanning electron micrograph of gold-coated scum. The length of the white lines is 100 μm.

Fig. 3. Scanning electron micrograph of carbon-coated scum. The white lines represent 10 μm.

elements present, and examined with a Jeol JSM-T200 scanning electron microscope. Figure 2, a photograph of a piece of scum magnified some 400 times, shows cracks in the material and some white particles resting on its surface. These white particles were magnified 1500 times (Fig. 3) and their spectrum revealed a high concentration of calcium with smaller amounts of manganese, phosphorus and other elements (Fig. 4). This suggested that the white particles were mainly $CaCO_3$. Some of the scum was therefore treated with 0.05 mol dm^{-3} HCl for 4 h to remove the calcium carbonate; bubbles of gas, presumably CO_2, were seen to escape from the surface. The solid was recovered by filtration, thoroughly washed and dried at 80°C. An electron micrograph of the treated material, enlarged some 400 times, is shown in Fig. 5. The resulting SEM spectrum gave no peak for calcium or for any other metal. Nor was any calcium seen in a check analysis of an Araldite glue section, only a small aluminium peak, presumably due to the underlying metal. The conclusion reached from these experiments is that tea scum is an organic material to which particles of $CaCO_3$ are attached.

Solid state NMR

For solids, high resolution proton-NMR gives poor results while calcium-NMR is even more difficult because of the extremely small abundance of the ^{43}Ca isotope (Groombridge, C. J., pers. commun., 1990). However, weak ^{13}C signals were observed with a Bruker MSL 300 NMR spectrometer by cross-polarization from protons. A peak at 169 ppm was assigned to $CaCO_3$ (Lauterbur, 1958). Other small peaks seen at 106 and 30.8 ppm could be attributed, respectively, to unsaturated carbon linkages and to methyl or methylene groups.

Fourier transform infrared spectroscopy

Pellets made from 15 g dried Spectrosol (BDH) KBr and 6 mg tea scum were examined with a Perkin Elmer 1720 infrared Fourier transform spectrophotometer.

Figures 6 and 7 show the resulting spectra of original and of HCl-treated scum, respectively. Both spectra possess a strong peak near 3417 cm^{-1}, due mainly to polymeric —O—H stretching. A much smaller peak at the same wavenumber for a pellet of KBr alone arose from a minor water impurity. The peaks at 2924 cm^{-1} in the two scum spectra can be ascribed to C—H stretching. The large peak at 1615 cm^{-1} in Fig. 6 indicates an ionic carbonyl stretch, almost certainly produced by $CaCO_3$. Removal of the calcium carbonate with HCl reveals, in Fig. 7, two smaller peaks which were previously covered up. The peak at 1717 cm^{-1} is a typical C=O stretch while that at 1622 cm^{-1} could be due to C=C or C=N stretch. The broad peak around 1200 cm^{-1} suggests complex phenolic absorption.

The FTIR analysis therefore shows that, apart from calcium carbonate, tea scum contains polymeric —OH groups, carbonyl groups and other unsaturated groups. This is not unexpected since the theaflavins and thearubigins in black tea are polyphenolic compounds. One source of the carbonyl groups could lie in the gallates known to be associated with theaflavin (Graham, 1983).

MALDI mass spectrometry

Tea scum, being involatile and insoluble in any of the solvents tried, could not be analysed by conventional mass spectrometric methods. It proved possible, however, to obtain an estimate of its molecular mass by the technique of matrix-assisted UV-laser desorption/ionisation mass spectrometry known as MALDI (Karas *et al.*, 1987, 1990). In this technique the sample is mixed with a suitable matrix substance and is then irradiated by a high intensity laser pulse in a mass spectrometer. After several trial experiments, 3-nitrobenzyl alcohol (3-NBA) was found to be a suitable matrix for tea scum. The untreated scum partially dissolved in 3-NBA while the HCl-treated scum did not. The untreated scum then required much lower laser power densities than the HCl-treated material.

An example of a MALDI spectrum of untreated tea scum is shown in Fig. 8, together with the background spectrum of pure 3-NBA. Each spectrum is the average of 10 shots. The difference spectrum gives a flat maximum at around 1100 daltons. The difference spectrum of another independent experiment also showed a flat peak around 1100 daltons, while a third experiment displayed a small peak at 500 and a larger broad peak at c. 2100 daltons. Two similar experiments with HCl-treated scum, after the appropriate 3-NBA correction, yielded flat maxima around 1050 and 1100, respectively. These broad spectra were quite different from the sharp peaks normally observed by the MALDI technique (Karas *et al.*, 1990) and so suggest that the material is heterogeneous in nature. Despite the wide spread of values, we shall adopt the average rounded figures of 1400 daltons for the untreated scum and 1100 for the HCl-treated material for the purpose of evaluating the empirical formulae below.
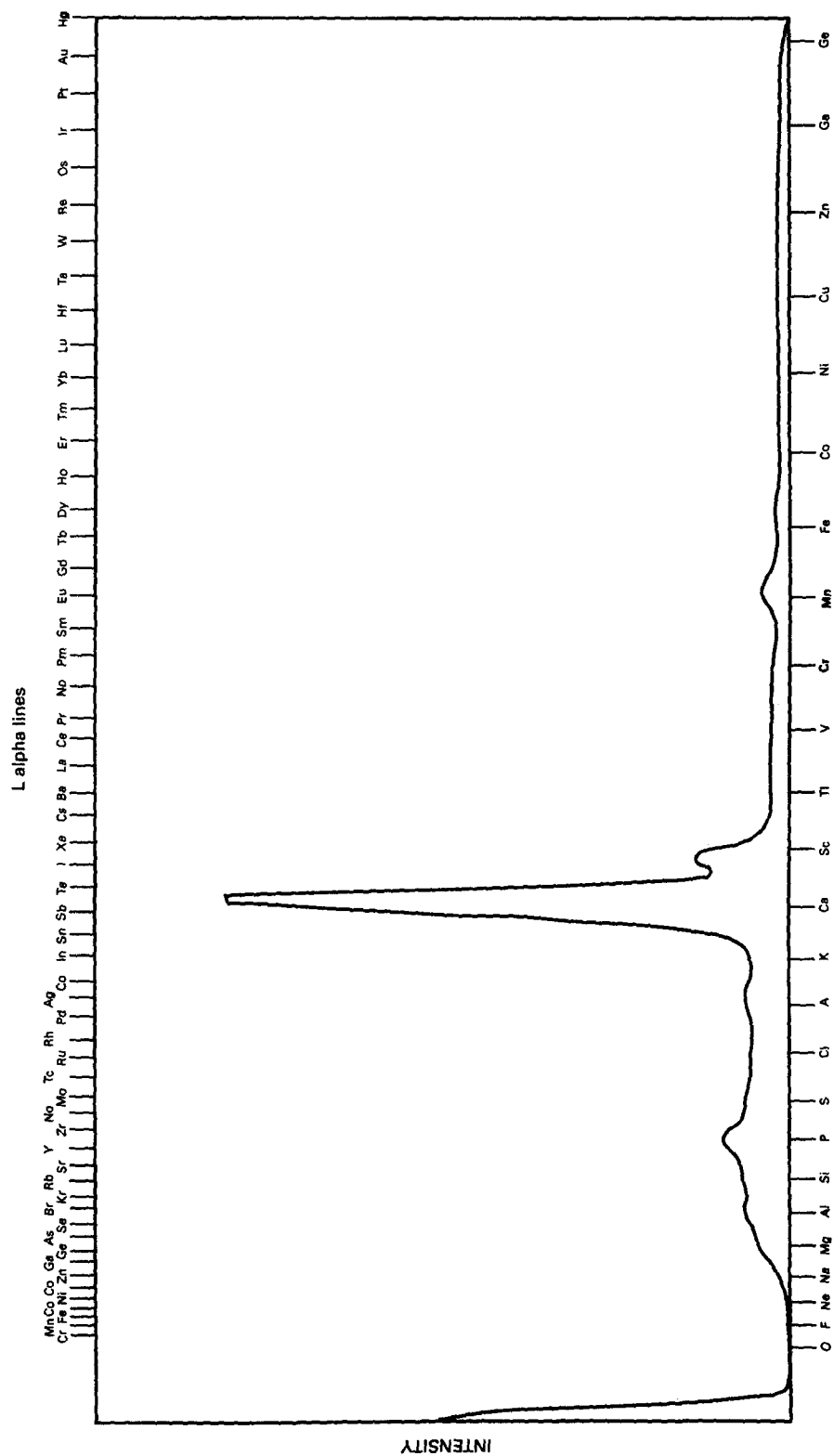
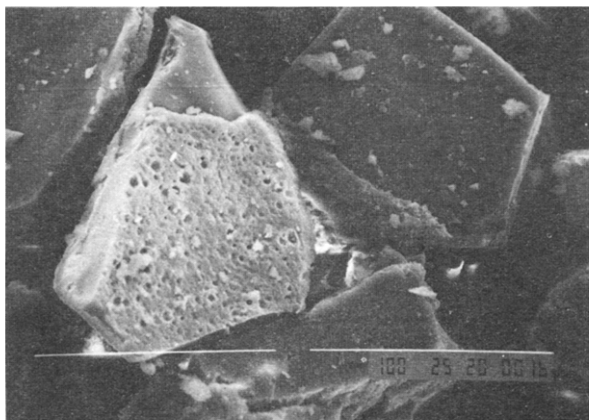**Fig. 4.** SEM spectrum of the white particles on tea scum (cf. Fig. 3).

Fig. 5. Scanning electron micrograph of HCl-treated scum. The length of the white lines is 100 μm.

Chemical microanalysis

In order to establish whether the composition of the scum varied with time, three series of runs were carried out with standard tea infusions which had been allowed to stand at 80°C for 15 min, 1 h and 4 h, respectively. Half the 1 and 4 h samples were then treated with 0.1 mol dm^{-3} hydrochloric acid for 30 min to dissolve any inorganic carbonates and hydroxides. The amount of 15 min scum gathered even after many experiments was, however, only large enough to allow the untreated material to be analysed.

The microanalytical results are summarised in Table 1. Calculations based on the Thames Water plc analysis of the London mains water and on the mineral content of black tea infusions (Natesan & Ranganathan, 1990) show that virtually all the calcium and sodium originated in the water, the potassium, manganese and aluminium came almost entirely from the tea leaf, while magnesium was provided in comparable amounts by both sources. Treatment with an HCl solution had removed all but a tiny amount of calcium from the tea scum, consistent with the metal ions being present in the form of insoluble carbonates and hydroxides rather than as integral components of the organic scum
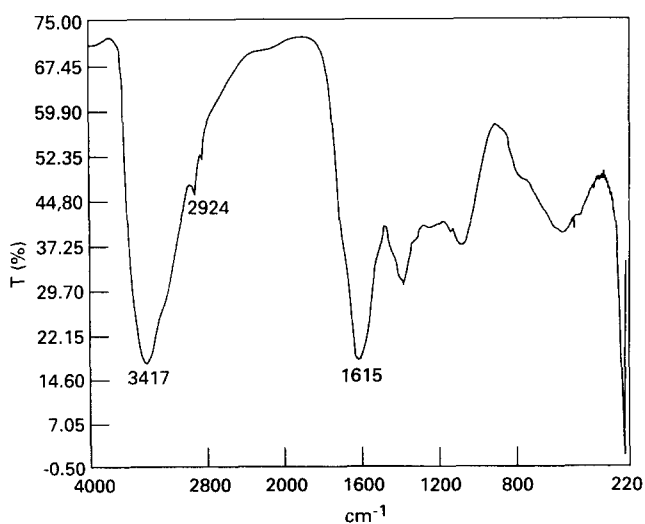

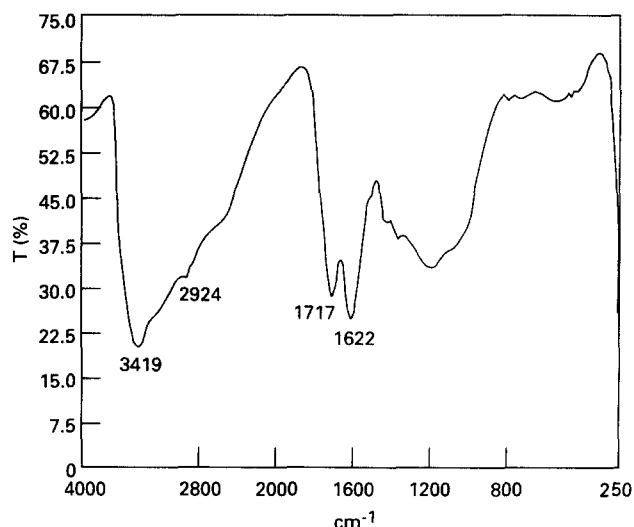**Fig. 6.** FTIR spectrum of tea scum.

Fig. 7. FTIR spectrum of HCl-treated tea scum.

matrix. It is interesting to note that the percentages of calcium and the other metals in the scum increased with time.

Inspection of the results in Table 1 shows that the composition of the 15 min scum is quite different from those of the 1 and 4 h scums, which are broadly similar. The percentages of all the major elements analysed (C, H and Ca) are much less in the 15 min material which must, therefore, contain a much higher percentage of oxygen. Its molar mass may also differ; taking it to be 1000 g, for instance, leads to the empirical formula:

$$C_{19.7}H_{26.1}O_{42.8}Ca_{0.85}(N_{0.30}Mg_{0.07}Mn_{0.16}Na_{0.07}K_{0.06})$$
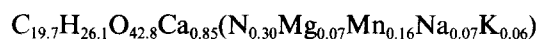
where the minor constituents have been bracketed. Combining all the divalent metals (Ca, Mg and Mn) together and calling them M gives $M_{1.08}$ in place of $Ca_{0.85}$.

An average of the 1 and 4 h results, together with the molar mass of 1400 g adopted above, leads to the empirical formula:

$$C_{46.2}H_{53.0}O_{41.8}Ca_{2.30}(N_{0.50}Mg_{0.22}Mn_{0.20}Na_{0.25}Al_{0.08})$$

with the divalent metals represented as $M_{2.72}$. Comparison with the 15 min formula suggests dimerisation with
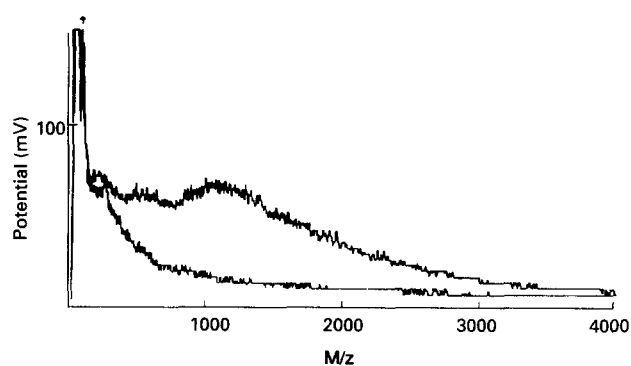

Fig. 8. MALDI spectrum of untreated tea scum, together with the spectrum of pure 3-NBA (lower curve), both at low laser power density. It is likely that $z=1$ so that m/z will give the molecular mass.

**Table 1. Analyses (in wt%) of tea scums allowed to form for various periods at 80°C**

| Element (uncertainty)	Untreated			HCl-treated	
	15 min	60 min	240 min	60 min	240 min
C (±0·3)	23·66	40·38	38·87	50·68	51·70
H (±0·3)	2·63	4·04	3·59	3·50	3·44
N (±0·1)	0·42	0·53	0·46	0·65	0·63
P	<0·6	<0·4	<0·4	<0·4	<0·4
S	<0·3				<0·3
Cl		<0·05			<0·05
Ca (±0·1)	3·41	6·06	7·14	0·04[a]	0·14[a]
Mg[b]	0·16	0·36	0·42	<0·1	<0·1
Na[b]	0·16	0·39	0·44	<0·05	<0·05
K[b]	0·24	<0·1	<0·1	<0·1	<0·1
Al[b]	<0·15	0·15	0·14	<0·1	<0·1
Mn[b]	0·88	0·92	0·64	<0·1	<0·1
Fe[b]	<0·15	<0·1	<0·1	<0·1	<0·1

[a] ±30% relative.
[b] ±2% relative.

time, but because no MALDI experiments were carried out with the 15 min scum such an interpretation is necessarily tentative. There is also an inference of much stronger initial oxidation of the organic material since the O:C ratio is far higher in the 15 min scum.

If it is assumed that the divalent metals in the 1 and 4 h scums are all present in the form of MCO_3, the formula of the organic part of the scum becomes

$$C_{43.5}H_{53.0}O_{33.6}(N_{0.50})$$
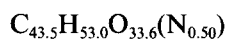
This can be compared with the empirical formula of the treated scum, also based on an average of the 1 and 4 h compositions together with the adopted molar mass of 1100 g, namely

$$C_{46.9}H_{37.8}O_{30.7}(Ca_{0.10}N_{0.50})$$
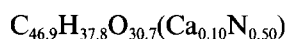
The number of carbon atoms can easily be reconciled since the molar masses of both types of scum span a wide range. However, the organic part of the original scum clearly contains a higher percentage of oxygen and a much higher percentage of hydrogen. This suggests that some of the metal compounds in the untreated scum may be hydroxides rather than carbonates and may contain water of crystallisation.

The two formulae for the organic part of the scum bear some resemblance to several known tea compounds derived from theaflavin or thearubigin. Among these are theaflavin digallate ($C_{43}H_{32}O_{20}$) (Graham, 1983), dimerised theaflavic acid ($C_{21}H_{16}O_{10}$) (Coxon et al., 1970), substance A ($C_{44}H_{34}O_{22}$) in Table III of the paper by Vuataz and Brandenberger (1961), and the recently reported thearubigin fraction theafulvin (Bailey et al., 1992), which displayed an ion with m/z=970 in Thermospray spectra leading to a formula $C_{40}H_{39}O_{<28}M_x$. All these substances contain around 40 carbon atoms and have molecular weights of the order of 10^3 g mol^{-1}, but possess smaller percentages of oxygen than the scum. Two other similarities are worth mentioning. The treated scum decomposed, but did not melt at 214°C,

which agrees with the m.p. of theaflavic acid (215°C decomp.) and with the behaviour of the crystals of Vuataz and Brandenberger (1961), which decomposed violently at 215°C but did not melt. This last phenomenon, however, was believed to be due to the molecule having crystallised with two molecules of ether. The second point concerns the presence of a small percentage of nitrogen. Several thearubigin workers, but not Bailey et al. (1992), have reported that their material contained some nitrogen. Brown et al. (1969) ascribed it to the presence of caffeine, while Vuataz and Brandenberger (1961) had earlier written that their 0.55% nitrogen could not be accounted for by either caffeine or amino acids. Table 1 shows that untreated tea scum contained c. 0.5% nitrogen and HCl-treated scum contained c. 0.6%. The origin of tea scum is discussed further in a following paper (Spiro & Jaganyi, 1994).

SUMMARY

The tea scum obtained in the present work corresponds to the second or enhanced type of scum of Kooijmans (1940). No evidence whatever was found for Kooijmans' first kind of scum: there was no sign of any surface film on infusing tea in distilled water and the properties of our scum, as well as the kinetics of its formation (Spiro & Jaganyi, 1994), do not agree with his descriptions of it. It may be that his tea contained a small amount of some oily impurity which floated to the surface of his infusions.

The physicochemical measurements we have carried out show the scum to be composed of an amorphous, high molecular weight organic material together with calcium carbonate and small amounts of magnesium and manganese carbonates or hydroxides derived partly from the hard water used and partly from the tea leaf itself. The organic matrix is complex and possibly polymeric and more research is needed to establish its exact precursors.

ACKNOWLEDGEMENTS

REFERENCES

Bailey, R.G., Nursten, H.E. & McDowell, I. (1992). Isolation and analysis of a polymeric thearubigin fraction from tea. J. Sci. Food Agric., 59, 365–75.

Brown, A.G., Eyton, W.B., Holmes, A. & Ollis, W.D. (1969). Identification of the thearubigins as polymeric proanthocyanidins. Nature, 221, 742–4.

Coxon, D.T., Holmes, A. & Ollis, W.D. (1970). Theaflavic and epitheaflavic acids. Tetrahedron Lett., 60, 5247–50.

Graham, H. (1983). Tea. In Kirk–Othmer Encyclopedia of

Chemical Technology (Vol. 22, 3rd edn), ed. M. Grayson & D. Eckroth. Wiley, New York, USA, pp. 628–44.

Karas, M., Bachmann, D., Bahr, U. & Hillenkamp, F. (1987). Matrix-assisted ultraviolet laser desorption of non-volatile compounds. *Int. J. Mass Spectrom. Ion Processes*, 78, 53–68.

Karas, M., Bahr, U., Ingendoh, A., Nordhoff, E., Stahl, B., Strupat, K. & Hillenkamp, F. (1990). Principles and applications of matrix-assisted uv-laser desorption/ionization mass spectrometry. *Anal. Chim. Acta*, 241, 175–85.

Kooijmans, J. (1940). Is de samenstelling van leidingwater van invloed bij de vliesvorming op thee? *Water (Neth.)*, 24, 65–7.

Lauterbur, P.C. (1958). Anisotropy of the C^{13} chemical shift in calcite. *Phys. Rev. Lett.*, 1, 343–4.

Natesan, S. & Ranganathan, V. (1990). Content of various elements in different parts of the tea plant and in infusions of black tea from southern India. *J. Sci. Food Agric.*, 51, 125–39.

Roberts, E.A.H. & Smith, R.F. (1963). The phenolic substances of manufactured tea. IX. The spectrophotometric evaluation of tea liquors. *J. Sci. Food Agric.*, 14, 689–700.

Schurer, D. (1960). Verband tussen de kwaliteit van een thee-infuus en de hardheid van water. *Voeding*, 21, 605–11.

Spiro, M. & Jaganyi, D. (1994). Kinetics and equilibria of tea infusion. Part 11. The kinetics of the formation of tea scum. *Food Chem.*, 49, 359–65

van Schaik, T.F.S.M. (1953). Vliesvorming op thee. *Voeding*, 14, 509–13.

Vuataz, L. & Brandenberger, H. (1961). Plant phenols. III. Separation of fermented and black tea polyphenols by cellulose column chromatography. *J. Chromatogr.*, 5, 17–31.