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Esterification of higher fatty acids by a novel strong solid acid

Atsushi Takagaki [a], Masakazu Toda [a], Mai Okamura [a], Junko N. Kondo [a],
Shigenobu Hayashi [b], Kazunari Domen [c], Michikazu Hara [a,*]

[a] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[b] Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[c] Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-7656, Japan

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Abstract

Carbon material prepared from D-glucose has been examined as a solid acid catalyst. Sulfonation of incompletely carbonized D-glucose results in amorphous carbon consisting of small polycyclic aromatic carbon sheets with high density of SO_3H groups. The carbon material exhibits remarkable catalytic performance for the esterification of higher fatty acids. This can be attributed to high density of SO_3H groups with strong acidity in the material.

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1. Introduction

Esters are essential chemicals that are widely used in the chemical industry. Many industrial esterification processes are carried out in the presence of strong Brønsted acid catalysts such as sulfuric acid or *p*-toluenesulfonic acid. However, such homogeneous acids are not environmentally benign and require special processing in the form of neutralization involving costly and inefficient catalyst separation from homogeneous reaction mixtures. This results in substantial energy wastage and the production of large amounts of chemical waste. Replacing such conventional ‘‘homogeneous Brønsted acids’’ with recyclable solid acids is a most promising solution to this problem, and the potential of these solid acids has been studied extensively [1–8]. Inorganic-oxide solid acids such as zeolite and niobic acid (providing acidic OH groups) have low densities of effective acid sites and thus cannot achieve adequate performance in acid-catalyzed reactions in the presence of water as a replacement for homogeneous Brønsted acids in esterification, hydrolysis and hydration. Although strong acidic cation-exchangeable resins such as perfluorosulfonated ionomers have sufficient SO_3H groups as strong acid sites even in water [9–12], these resins are expensive and the acid activities are still much lower than achievable by homogeneous Brønsted acids [7]. These limitations have restricted the practical utility of acidic cation-exchangeable resins.

Sulfonated naphthalene carbonized at 200–250 °C has been shown to function as an active and stable solid catalyst for ethyl acetate formation, an easy acid-catalyzed reaction [13]. However, as this material is soft aggregate of polycyclic aromatic carbon with sulfonic acid groups (SO_3H) rather than rigid carbon material, the sulfopolycyclic aromatic compounds are leached from the solid by liquid-phase reactions over 100 °C or with higher fatty acids as surfactants, resulting in rapid degradation of catalytic activity. Here, a new strategy is adopted: sulfonation of incompletely carbonized natural organic material. Incomplete carbonization of natural products such as sugar, starch and cellulose results in a rigid carbon material composed of small polycyclic aromatic carbon sheets in a three-dimensional sp^3-bonded structure. Sulfonation of such carbon materials is thus expected to afford a highly stable solid with a high density of active sites, allowing high-performance catalysts to be prepared from common natural products.

2. Experimental

2.1. Preparation of carbon material

The carbon materials can be readily prepared by sulfonation of incompletely carbonized-glucose. In this

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* Corresponding author. Tel.: +81 45 924 5239; fax: +81 45 924 5282.
E-mail address: mhara@res.titech.ac.jp (M. Hara).

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synthesis, D-glucose was incompletely carbonized at low temperature to cause pyrolysis of D-glucose and form small polycyclic aromatic carbon. SO_3H groups were introduced into the aromatic carbon rings of the amorphous carbon sheets. In a typical synthesis, 20 g of D-glucose was heated for 15 h at 673 K under N_2 flow to produce a brown-black solid. The solid was then ground to a powder and heated in 200 mL of concentrated H_2SO_4 (>96%) or 150 mL of fuming sulfuric acid (15 wt.% SO_3) at 423 K under N_2. After heating for 15 h and then cooling to room temperature, 1000 mL of distilled water was added to the mixture to form a black precipitate. The precipitate was washed repeatedly in hot distilled water (>353 K) until impurities such as sulfate ions were no longer detected in the wash water.

2.2. Esterification of highly fatty acid with ethanol in liquid phase

Esterification of higher fatty acids was carried out at 353 K in an ethanol–oleic acid ($C_{17}H_{33}COOH$) mixture (ethanol, 0.10 mol; oleic acid, 0.010 mol) and ethanol–stearic ($C_{17}H_{35}COOH$) acid mixture (ethanol, 0.10 mol; stearic acid, 0.010 mol; toluene, 10 mL) under Ar atmosphere. All tested catalysts except sulfuric acid were evacuated at 373–453 K for 1 h prior to reaction to remove adsorbed water, and 0.2 g of each catalyst was used in the reactions. The liquid phase during reaction was analyzed by a gas chromatograph mass spectrometer (GC–MS; GCMS-QP5050A, Shimadzu) with capillary columns. For comparison, the catalyses for 0.2 g of concentrated sulfuric acid (>96%), protonated-Nafion (NR50), niobic acid ($Nb_2O_5 \cdot nH_2O$, CBMM Co. Ltd.; BET surface area, 128 $m^2\,g^{-1}$) and H-mordenite (H-MOR, $SiO_2/Al_2O_3 = 18.3$, JRC-Z-HM20; BET surface area, 205 $m^2\,g^{-1}$) were also examined.

2.3. Characterization

The samples were characterized by X-ray diffraction (XRD; Rint 2000, Rigaku), X-ray photoelectron spectroscopy (XPS; ESCA 3200, Shimadzu), and ^{13}C magic angle spinning nuclear magnetic resonance (^{13}C MAS NMR; Bruker ASX200 spectrometer, Larmor frequency 50.3 MHz, spin rate 4.0 kHz).

Acid densities of the prepared samples were estimated by neutralization titration using NaOH aqueous solution. The acidities were examined using a color-producing reagent. As the coloration of the reagents cannot be observed by inspection on these black carbon materials, the acidity was examined by ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS; V560, JASCO). A mixture of the carbon material (0.2 g) and $BaSO_4$ (a reference material for DRS measurement, 1.0 g) powder was evacuated at 423 K for 1 h to remove adsorbed water. In an Ar-filled glove box, the mixture was packed into a sealable quartz cell, and benzene (with or without color-producing reagent) was then added to the cell. The DRS of the mixture in each benzene solution was measured without exposure to air. The DRS of the color-producing reagent in the presence of the carbon material was obtained by subtracting the spectrum for the mixture in pure benzene from that of the mixture in the benzene solution solving the color-producing reagent. The DRS for each color-producing reagent was also observed using $BaSO_4$ in benzene with and without the color-producing reagent in a similar manner.

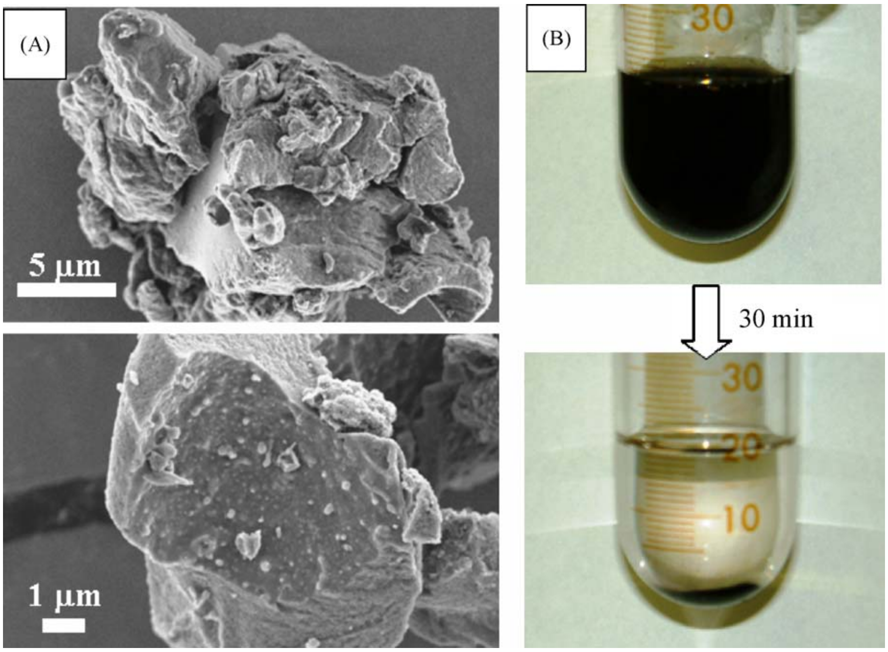

Fig. 1. (A) Scanning electron microscope (SEM) images and (B) photographs of the carbon material in distilled water with and without stirring. Solid acid powder is dispersed in distilled water upon stirring and precipitates when let stand for 30 min.

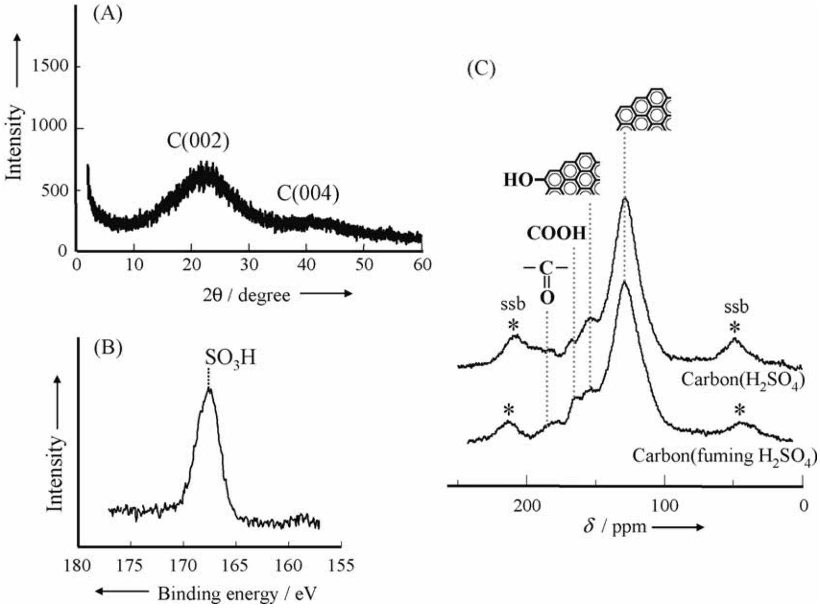

Fig. 2. Powder XRD pattern, XPS spectrum and ^{13}C MAS NMR spectra for the carbon materials prepared from D-glucose. (A) Powder XRD pattern for carbonized D-glucose sulfonated by fuming H_2SO_4 (Carbon(fuming H_2SO_4)). (B) XPS for Carbon(fuming H_2SO_4). (C) ^{13}C MAS NMR spectra for carbonized D-glucose sulfonated by concentrated H_2SO_4 and fuming H_2SO_4 (Carbon(H_2SO_4), Carbon(fuming H_2SO_4)). Spinning sidebands (ssb) appear at ca. 50 and 210 ppm.

3. Results and discussion

3.1. Structure of carbon material

The SEM images of the prepared carbon material are shown in Fig. 1. The powder, irregular particles with grain sizes larger than 1 μm, can be readily dispersed in solvents by stirring, and precipitates rapidly when not stirred as shown in Fig. 1.

Fig. 2 shows the powder X-ray diffraction (XRD) pattern, X-ray photoelectron spectroscopy (XPS) spectrum and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra for the samples. The powder X-ray diffraction (XRD) pattern for the carbon material after sulfonation exhibits broad, weak diffraction peaks due to carbon (0 0 2) and (0 0 4), attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion [14]. In the XPS for these carbon materials, an S 2p peak was observed at 168 eV, assigned to SO_3H groups, meaning that all S atoms in the carbon materials are contained in SO_3H groups. The atomic ratios of S/C in carbonized D-glucose sulfonated in concentrated H_2SO_4 (Carbon(H_2SO_4)) and fuming H_2SO_4 (Carbon(fuming H_2SO_4)) were estimated to be 0.01 and 0.04, respectively, on the basis of S 2p and C 1s peaks. This is consistent with the sample compositions given by elementary analysis (see Table 1). The ^{13}C MAS NMR spectra for the samples exhibit the resonance peaks at 130, 155, 165 and 180 ppm attributable to aromatic carbon atoms, phenolic OH, COOH and carboxyl groups (–CO– in COOH groups), respectively [15,16]. The resonance due to aromatic carbon with SO_3H groups (ca. 140 ppm) [15] is obscured in these two samples by the broad peaks due to aromatic carbon atoms (130 ppm) and COOH groups (155 ppm). These results indicate that the carbon materials are amorphous carbon consisting of polycyclic aromatic carbon sheets with phenolic OH and COOH groups in addition to not a little SO_3H groups (0.7–1.2 mmol g^{-1}, see Table 1) as illustrated in Fig. 3.

3.2. Higher fatty acid esters formation by solid acid catalysts

The acid catalysis of these samples was demonstrated through ethyl oleate ($C_{17}H_{33}COOC_2H_5$) formation from oleic

Table 1
Catalytic activities of tested samples (0.2 g) at 353 K

Catalyst (composition)	Surface area (m^2 g^{-1})	Acid density (mmol g^{-1})		Rate of ethyl oleate formation (μmol min^{-1})
		Total	SO_3H	
Carbon(H_2SO_4) ($CH_{0.45}S_{0.01}O_{0.39}$)	2	1.4	0.7	44
Carbon(fuming H_2SO_4) ($CH_{0.29}S_{0.03}O_{0.41}$)	1	2.5	1.2	86
Protonated-Nafion (NR50)	<0.1	0.9	0.9	12
Niobic acid ($Nb_2O_5 \cdot nH_2O$)	128	0.4	–	–
H-MOR	399	1.0	–	–
H_2SO_4		20.4		156

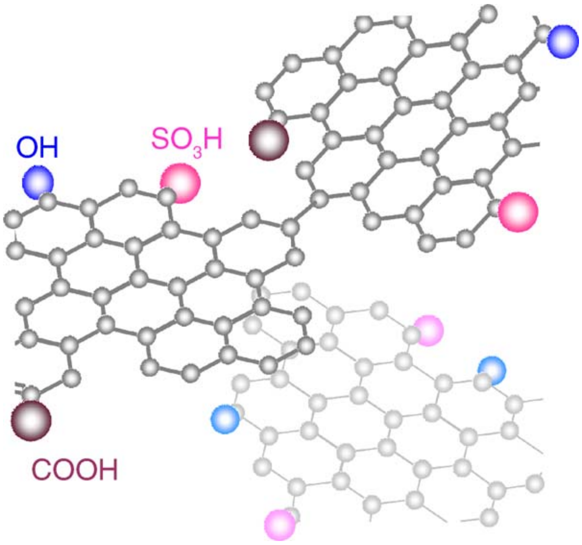

Fig. 3. Proposed schematic structure of the carbon materials prepared from D-glucose. The materials are amorphous carbons consisting of polycyclic aromatic carbon sheets with phenolic OH and COOH groups in addition to SO$_3$H groups.

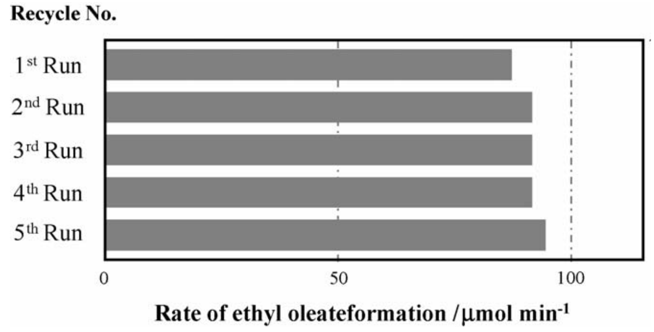

Fig. 4. Recycling of carbon material (Carbon(fuming H_2SO_4)) in ethyl oleate formation.

acid and ethyl stearate ($C_{17}H_{35}COOC_2H_5$) formation from stearic acid as examples of the esterification of higher fatty acids. Oleic and stearic acids are the main ingredients in various vegetable oils such as rapeseed oil, palm oil, soybean oil and sunflower oil, and the higher fatty acid esters are used as high-grade biodiesel. The compositions, surface areas, acid densities [17] and catalytic activities (rate of ethyl oleate formation) for 0.2 g of the prepared samples are summarized in Table 1. For comparison, the results for 0.2 g of concentrated H_2SO_4 (>96%), protonated-Nafion (NR50), niobic acid ($Nb_2O_5 \cdot nH_2O$) and H-mordenite (H-MOR) are also shown. Protonated-Nafion, a polymer-based strong solid acid, exhibits very high activity for reactions involving thermostable solid acids [7,9–12]. Niobic acid and H-MOR are typical inorganic oxide strong solid acids that are widely used in industrial acid-catalyzed reactions. The carbon material prepared in this study exhibits remarkable catalytic performance for ethyl oleate formation, much higher than those for conventional solid acids, including Nafion. The performance for the esterification of stearic acid was similar to that for ethyl oleate formation. The conventional solid acids have much lower activities for the esterification of higher fatty acids than H_2SO_4, while the activity of Carbon(fuming H_2SO_4) exceeds half that of concentrated H_2SO_4. The carbon material sulfonated in fuming H_2SO_4 (Carbon(fuming H_2SO_4)) posses twice higher catalytic activity than the carbon material sulfonated in concentrated H_2SO_4 (Carbon(H_2SO_4)) because the SO_3H density of the former is twice that of the latter. This can be attributed to the strong sulfonation and consumption of H_2O in fuming H_2SO_4, where generated H_2O is converted to H_2SO_4 by SO_3, forcing the equilibrium of sulfonation ($Ar–H + H_2SO_4 \leftrightarrow Ar–SO_3H + H_2O$) toward the formation of SO_3H groups. Reactions in the presence of these carbon materials reached equilibrium within 4–10 h, and the samples were recovered by simple decantation. No decrease in activity or leaching of SO_3H groups from the materials to the reaction solution were observed, even for samples reused up to five times as shown in Fig. 4. Apparently, the carbon materials have clear potential for use as a replacement for sulfuric acid catalyst for the higher fatty acid ester formation.

Although there is no significant difference in SO_3H density between the carbon materials and Nafion, the carbon materials exhibit higher catalytic activities. One possible explanation for that might be attributed to acid strength of the samples. To clarify the difference in activity, the acidities were examined using a color-producing reagent. As the coloration of the reagents cannot be observed by inspection on these black carbon materials, the samples were examined by ultraviolet-visible diffuse reflectance spectroscopy (DRS). Fig. 5 shows the DRS spectra for Carbon(fuming H_2SO_4) coated with the color-producing reagents after subtraction of the reflection due to the carbon material. The spectra for the color-producing reagents are also shown for comparison. A broad absorption band

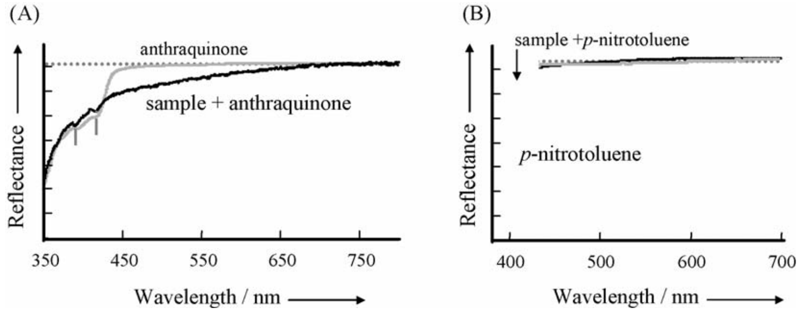

Fig. 5. DRS of Carbon(fuming H_2SO_4) with (A) anthraquinone and (B) *p*-nitrotoluene. The reflection due to the carbon material is cancelled in the spectra. The grey lines are reflections of anthraquinone and *p*-nitrotoluene.

appears at 450–600 nm in the spectrum for Carbon(fuming H_2SO_4) with anthraquinone, attributable to the yellow coloration of anthraquinone in strong acid ($pK_a \leq -8.2$) corresponding to concentrated H_2SO_4 of greater than 90 wt.%. The yellow coloration of *p*-nitrotoluene ($pK_a \leq -11.4$) is not observed, indicating that the pK_a of Carbon(fuming H_2SO_4) is in the range of approximately −11 to −8, comparable to that of concentrated H_2SO_4. The coloration of the color-producing reagents on Carbon(H_2SO_4) was also the same as that of Carbon(fuming H_2SO_4). As a result, the present carbon materials have weaker acidities than Nafion ($pK_a = -12$), and the high catalytic performance of the carbon materials are not due to the density of SO_3H groups or the acid strength. Another possible origin of the high activity is phenolic OH and COOH groups on the catalyst. In general, these functional groups cannot catalyze the esterification because of the weak acidities, while the functional groups attached to such a carbon material, especially COOH groups, might have strong acidities and contribute to the high catalytic activity. It is also probable that these functional groups increase hydrophilicity of the carbon material, resulting in the improvement of accessibility for hydrophilic reactants. Further detailed study will be necessary to determine how these functional groups contribute to the reaction.

4. Conclusion

Amorphous carbon with not a little SO_3H groups was shown to exhibit strong potential for use as a replacement for sulfuric acid catalyst in the esterification of higher fatty acids. Many industrially important chemicals—petrochemicals, raw materials for polymers and fibers, drugs, food additives—have been produced by using ‘‘liquid acid catalysts’’, resulting in huge energy wastage and annual chemical wastes over 20 million tons. Thus, we expect that this approach is not only available for biodiesel production but will have fundamental implications in the eco-friendly production of chemicals through acid-catalyzed reactions.

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References

[1] P.T. Anastas, M.M. Kirchhoff, Acc. Chem. Res. 35 (2002) 686.
[2] J.M. DeSimone, Science 297 (2002) 799.
[3] B. Harton, Nature 400 (1999) 797.
[4] P.T. Anastas, J.B. Zimmermann, Environ. Sci. Technol. 37 (2003) 94A.
[5] J.H. Clark, Acc. Chem. Res. 35 (2002) 791.
[6] M. Misono, CR Acad. Sci. Ser. II: Chim. 3 (2000) 471.
[7] T. Okuhara, Chem. Rev. 102 (2002) 3641.
[8] K. Smith, G.A. El-Hiti, A. Gamal, A.J. Jayne, K. Butters, Org. Biomol. Chem. 1 (2003) 1560.
[9] G.A. Olah, P.S. Iyer, G.K.S. Prakash, Synthesis 7 (1986) 513.
[10] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, Nature 416 (2002) 304.
[11] K. Wilson, A.F. Lee, D.J. Macquarie, J.H. Clark, Appl. Catal. A: Gen. 228 (2002) 27.
[12] E. Cano-Serrano, J.M. Campos-Martin, J.L.G. Fierro, Chem. Commun. 247 (2003) 246.
[13] M. Hara, T. Yoshida, A. Takagaki, T. Takata, J.N. Kondo, S. Hayashi, K. Domen, Angew. Chem. Int. Ed. 43 (2004) 2955.
[14] N. Tsubouchi, K. Xu, Y. Ohtsuka, Energy Fuels 17 (2003) 1119.
[15] R.M. Silverstien, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compound, 5th ed., John Wiley and Sons, Indianapolis, 1991, p. 218.
[16] X. Zhang, D.H. Solomon, Chem. Mater. 11 (1999) 384.
[17] Acid densities of the prepared samples were estimated by neutralization titration. As COOH and SO_3H groups were present in samples prepared from D-glucose, the acid densities estimated by neutralization titration are total amounts of these functional groups. According to XPS analysis, it is expected that all S atoms in the carbon materials are contained in SO_3H groups. The densities of SO_3H groups were thus estimated based on the S content in sample compositions determined by elemental analysis.