# Technical Report: Organic Residues from Egyptian Blue Anhydrite Duck Flasks and Other Anhydrite Vessels

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MANY CERAMIC AND STONE VESSELS now found in museum collections were originally made to hold organic materials, such as foodstuffs, cosmetics, and perfumes. These organic materials can penetrate into the walls of the vessels, so that residues of the original contents may actually survive even when there is no visible remnant of them. By using strong organic solvents, one can at least partially extract residues trapped in the ceramic or stone and then analyze the extracted compounds. An analysis cannot be expected to provide an accurate view of the original contents for many reasons. The solvent will not necessarily extract all types of organic materials, and the analytical technique utilized to identify the organic materials will not necessarily analyze all of the compounds found in the solvent extract. More important, aging results in the destruction of many organic materials and changes the compositions of others. Volatile components of the original contents may have been lost, and some components may also have been lost to the soil in which an object rested for an extended period of time prior to its excavation. Even given these limitations, analysis of the solvent extract provides a glimpse of the original contents.[1] This article presents analyses of solvent-extracted organic residues from sixteen anhydrite vessels. The extracts were analyzed by gas chromatography/mass spectrometry (GC/MS).[2]

Published studies of solvent extracts from ceramics frequently indicate that fatty acids are the major detectable compounds. Fatty acids occur in different types of materials, the major sources of which are vegetable oils and animal fats; fatty acids also occur in substantial amounts in beeswax. In fresh oils and fats, fatty acids are present mostly in the form of triglycerides. During aging, triglycerides can react to form larger polymeric molecules, or can break down into molecules, including free fatty acids and various smaller fragments. As a result of chemical reactions, the compositions of aged oils and fats are quite different from those of their fresh counterparts.[3] The typical methods of analyzing aged oils and fats do not detect polymeric material; instead, only fatty acids and small breakdown products are actually analyzed. The fatty acids in oils and fats are of two general types, unsaturated and saturated. Aged materials contain saturated fatty acids, which are fairly nonreactive, perhaps with only small amounts of unsaturated fatty acids (which are very reactive) remaining. The types and relative amounts of saturated fatty acids vary to some extent between oils from different sources and fats. Since the saturated fatty acids do not appear to be altered to a great degree during aging, their proportions in an ancient oil or fat will resemble their proportions in the fresh material; thus analysis permits some speculation on possible original sources.[4]

Some other major components of many aged oils and fats are dibasic acids. These acids, which are not present in fresh oils and fats, form during aging. Their abundances, relative to the saturated fatty acids, are not the same in all aged oils and fats; they provide another piece of information on which speculation about original source materials can be based. Oils can be divided into three general types: drying, semidrying, and nondrying. Thin films of drying oils rapidly solidify by chemical reactions when exposed to the air. These types of oils (which include linseed, walnut, and poppyseed) have been used for many centuries as binders in oil paints, but some (such as linseed) were known well before oil painting was developed. Semidrying oils partially solidify, while nondrying oils do not form solid films. Dibasic acids (the major one of which is azelaic acid) are abundant in aged drying oils, relative to the remaining saturated fatty acids; dibasic acids are very minor components of aged nondrying oils when compared with the saturated fatty acids. Thus the relative amounts of dibasic and saturated fatty acids give some indication of general oil type, although a specific type may not be able to be identified. Aged animal fats contain mostly saturated fatty acids.

Many other compounds besides fatty acids can also be detected in solvent extracts and may shed further




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light on the original contents of the vessel. Cholesterol, for example, would suggest the presence of animal fat. If the vessel being tested originally contained perfume, some compounds from the fragrant materials used in formulating the perfume could still be present.

Since relatively small amounts of material are being extracted from the object, the possibility of contamination from conservation treatment or handling needs to be kept in mind. All of the objects analyzed were intact and did not appear to have been treated in any way. High-purity solvent and carefully cleaned vials were utilized so that contamination from these sources would be negligible. However, traces of phthalates were found in nearly all of the extracts. These are common plasticizers used in plastic bags and could have been transferred to the objects from bags in which the stone objects may have been stored.

Many of the samples contained dozens of easily detectable individual compounds, not all of which have been identified at the time of writing of this paper. Nearly all of the predominant compounds in all the samples have been identified. Not surprisingly, these are mostly fatty acids and dibasic acids. Small amounts of other materials (beeswax and natural plant resins) were found in some vessels. Natural resins could have been components of perfumes, which were often made by mixing fragrant substances in oil or fat. No other plant extracts were specifically identified in any of the samples from the anhydrite vessels.

## Discussion of Results

Table 1 summarizes the results. Objects are listed in order of decreasing azelaic acid (diC9) content: azelaic acid is the major dibasic acid found in aged oils. Some general comments on the results are given below. Individual objects are referred to by the letter given to them in Table 1. Chromatograms of some of the samples are shown in Figures 1 and 2.

*Types of oils and fats.* The high azelaic acid levels in a few samples suggest that they contained semi-drying or drying vegetable oils. Duck flask A, which has a very high azelaic acid level, almost certainly contained a drying oil, which could perhaps have been linseed oil. The ratio of palmitic (C16) to stearic (C18) acids in this sample (2.5) is somewhat higher than is considered typical for linseed oil, but much closer to that of linseed than other common drying oils. Three other objects (B, C, and D) have relatively high azelaic acid levels (0.4–0.5), suggesting that they contained drying or perhaps semi-drying oil.

The other samples have low or negligible azelaic acid levels. These low levels suggest that the original contents were nondrying vegetable oils (olive oil is one example of such an oil), or possibly animal fat. The high amount of stearic acid found in two samples (J and O) is more suggestive of animal fat than of a vegetable oil. If animal in source, the possible source cannot be more specifically determined: for example, goat, sheep, beef, or goose is equally possible.

Palmitic and stearic acids are the major saturated fatty acids found in most oils and fats. Not surprisingly, they are the major ones found in nearly all these samples. Some samples contained rather large amounts of other saturated fatty acids. Six (G, H, I, K, L, and P) contained myristic (C14) acid at a level of 20 percent or more than of palmitic (C16) acid. Myristic acid is an important constituent of fish oils, and it is possible that these six objects contained such an oil. There does not appear to be any correlation between the type of oil or fat kept in a vessel and its shape: at least three different materials appear ot have been kept in the four duck flasks (A, G, H, and O) whose contents have been analyzed.

It also needs to be kept in mind that more than one type of oil or fat may have been stored in an object. Two of the objects (E and N) had more than one chamber in which material could be stored. In the case of both objects, extracts from the separate chambers were similar, suggesting that both chambers had been used to store the same material.

*Natural resins.* Very small amounts of one or two compounds that are found in aged conifer resins were detected in about half of the vessels (A, B, E, G, I, N, and P).[5] The most likely source of these compounds is a resin from a pine, larch, or fir tree. In one sample (N, sample from R chamber), a small amount of a third compound (sandaracopimaric acid) was also detected.[6] This compound is an abundant one in sandarac resin, as well as resins from juniper and cypress trees. It seems possible that two different resins were present in this vessel.

*Beeswax.* Samples from three objects (B, E, and N) may have contained beeswax.[7]

## Summary

With one exception (N), all the vessels appear to have contained an oil or fat. While specific types of oils cannot be identified, the analyses indicate that more than one type was involved. Some almost certainly con-

tained a drying oil, but most contained nondrying oils (or animal fat). In nearly half the objects that contained oil or fat, a conifer resin of some type (most likely pine, larch, or fir) was also found. One object contained beeswax and probably two types of conifer resins (N). It is not certain that this object contained oil or fat. Two other objects contained beeswax and a conifer resin, along with some oil (B and E).

## NOTES

1. Some recent studies of different types of organic residues in ceramics include the following: W. R. Biers, K. O. Gerhardt, and R. A. Braniff, "Lost Scents: Investigations of Corinthian 'Plastic' Vases by Gas Chromatography-Mass Spectrometry," *MASCA Research Papers in Science and Archaeology* 11 (1994) 59 pp.; S. Charters, R. Evershed, P. Blinkhorn, and V. Denham, "Evidence for the Mixing of Fats and Waxes in Archaeological Ceramics," *Archaeometry* 37 (1995) pp. 113–127; S. Charters, R. Evershed, L. Goad, A. Leyden, P. Blinkhorn, and V. Denham, "Quantification and Distribution of Lipid in Archaeological Ceramics: Implications for Sampling Potsherds for Organic Residue Analysis and the Classification of Vessel Use," *Archaeometry* 35 (1993) pp. 211–223.

2. Several milliliters of GC/MS-grade methylene chloride were swished around the inside of the object, then transferred to a 2- or 5-ml sample vial and the solvent evaporated to dryness. The dried residue, which usually included substantial inorganic material, was then mixed with 150–200 µl of a transesterification reagent, (m-trifluoromethylphenyl) trimethylammonium hydroxide, 0.2 N in methanol. The vial was capped and the solution heated to 50°C. for about five hours. The analyses were carried out the following day by gas chromatography/mass spectrometry (GC/MS). Usually 1 µl of the solution was injected into the instrument; if this proved to be too concentrated, a second run was carried out using a ~0.3 µl injection. Analyses were carried out on a Hewlett Packard 5890 capillary GC with an HP 5971A mass selective detector (MSD). Instrumental conditions were as follows: injection port temperature, 275°C., split/splitless inlet, operated in split mode (ratio–20:1); MSD interface temperature, 280°C.; oven program, 100°C. to 300°C. at 10°/minute. Column: Supleco PTE-5, 30 meter, 0.25 mm ID, 0.25 µm film thickness. The mass spectrometer was operated in scan mode, from 50–550 amu. Peaks were identified by their mass spectra, with reference to the Wiley Reference Library of Mass Spectra and various standards run in the laboratory.

3. J. S. Mills and R. White, *The Organic Chemistry of Museum Objects* (London, 2nd ed., 1994) pp. 34–45.

4. Attempts at identification are most likely to be successful if fairly substantial residues actually survive. One example is E. Morgan, C. Edwards and S. Pepper, "Analysis of the Fatty Debris from the Wreck of a Basque Whaling Ship at Red Bay, Labrador," *Archaeometry* 34 (1992) pp. 129–134. As this study shows, the saturated fatty acid composition of aged fats and oils also changes with aging, at least under certain conditions, and this means that the overall saturated fatty acid composition of an aged fat or oil cannot be expected to be precisely that of the fresh fat or oil from which it derived. How extensive the changes will be, however, cannot be predicted for most samples, including the extracts analyzed in the present project.

5. The specific compounds detected were the methyl esters of dehydroabietic acid and 7-oxodehydroabietic acid (results for individual samples are listed in Table 1). Both compounds are products of the oxidation of abietic acid. Abietic acid is found in many resins, particularly from the conifer family. Resins from trees of the Pinaceae family of the conifer group order (a family that includes pines, larches, spruces, and firs) are widespread and all contain important amounts of abietic acid. Abietic oxidation products may be all that remain readily analyzable in aged conifer resins (see Mills and White, *The Organic Chemistry of Museum Objects*, p. 100).

6. The specific compound detected is the methyl ester of sandaracopimaric acid. This compound is a major nonpolymeric component of resins from the Cupressaceae family of the conifer order, a family that includes *Tetraclinis articulata* (which produces the resin known as sandarac), as well as cypress and juniper trees. Of these, sandarac, from northern Africa, probably would have been the type most readily available in ancient Egypt. Little is known about the composition of highly aged resins from this genus, although the presence of sandaracopimaric acid in a 600-year-old resin varnish on an Italian painting has been taken as evidence for the presence of sandarac resin in the varnish (J. Dunkerton, J. Kirby, and R. White, "Varnish and Early Italian Tempera Paintings," in J. Mills and P. Smith, eds., *Cleaning, Retouching and Coatings* [London, 1990] pp. 63–69).

7. Beeswax that has been saponified, as was the case in the analyses carried out here, contains a large amount of palmitic acid and much smaller amounts of stearic acid and several others. Also present are straight-chain hydrocarbons and long-chain alcohols (the latter not readily analyzable by the particular procedure utilized here). The pattern of hydrocarbons and fatty acids with 20 or more carbon atoms is fairly distinctive for beeswax and permits its presence to be detected even when oils or fats are also present (see, for example, J. Mills and R. White, "The Mediums used by George Stubbs: Some Further Studies," *National Gallery Technical Bulletin* 9 [1985] pp. 60–64). A ratio of palmitic to stearic acid that is considerably lower than that of beeswax suggests than an oil or fat was mixed with the beeswax. Significant amounts of dibasic acids would also point to the admixture of a drying or semidrying oil.

TABLE 1. RESULTS OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSES OF METHYLATED METHYLENE CHLORIDE EXTRACTS

| Object | diC8 | diC9 | diC10 | C14 | C15 | C16 | C17 | C18 | C20 | C22 | C24 | C26 | Other compounds |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Museum of Fine Arts, Boston* | | | | | | | | | | | | | |
| ***A.*** *Duck flask (3)* 65.1749 | 0.33 | 1.67 | 0.09 | 0.04 | <0.01 | 1.00 | 0.01 | 0.41 | 0.08 | 0.04 | 0.03 | | Conifer resin (note 1) |
| *The Metropolitan Museum of Art, New York* | | | | | | | | | | | | | |
| ***B.*** *Vessel* 12.182.74 | 0.22 | 0.51 | 0.05 | 0.06 | 0.01 | 1.00 | 0.01 | 0.20 | 0.03 | 0.03 | 0.07 | | Beeswax, conifer resin (note 2) |
| ***C.*** *Pot with monkeys* 07.228.93 | 0.16 | 0.45 | 0.04 | 0.08 | 0.04 | 1.00 | 0.03 | 0.34 | 0.04 | 0.03 | 0.05 | | (See note 3) |
| ***D.*** *Lentoid flask* 10.176.53 | 0.13 | 0.43 | | 0.17 | | 1.00 | | 0.40 | | | | | (See note 4) |
| ***E.*** *Two monkeys (jars)* | | | | | | | | | | | | | |
| 12.182.77L | 0.08 | 0.16 | 0.01 | 0.02 | <0.01 | 1.00 | <0.01 | 0.12 | 0.01 | 0.01 | 0.04 | <0.01 | Beeswax, conifer resin (note 5) |
| 12.182.77R | 0.04 | 0.10 | <0.01 | 0.03 | <0.01 | 1.00 | 0.01 | 0.17 | 0.02 | 0.02 | <0.01 | <0.01 | Conifer resin (note 6) |
| ***F.*** *Pot with monkeys* 66.99.16 | 0.03 | 0.13 | | 0.03 | 0.01 | 1.00 | 0.01 | 0.17 | 0.03 | 0.01 | 0.01 | | (See note 7) |
| ***G.*** *Duck flask (9)* 10.176.51 | | 0.12 | | 0.33 | 0.07 | 1.00 | 0.05 | 0.40 | 0.04 | | | | Conifer resin (note 8) C12 acid present |
| ***H.*** *Duck flask (12)* 24.2.25 | 0.05 | 0.10 | | 0.26 | 0.07 | 1.00 | 0.05 | 0.62 | 0.06 | 0.08 | 0.04 | | (See note 9) |
| ***I.*** *Amphora* 10.176.46 | | 0.06 | | 0.36 | 0.10 | 1.00 | 0.07 | 0.44 | 0.05 | 0.04 | 0.07 | | Conifer resin (note 10) C12 acid present |
| ***J.*** *Fish flask* 10.176.52 | 0.02 | 0.05 | | 0.08 | 0.03 | 1.00 | 0.06 | 3.50 | 0.05 | 0.02 | 0.01 | | (See note 11) |
| ***K.*** *Bag-shaped jar* 10.176.48 | | 0.04 | | 0.46 | 0.09 | 1.00 | 0.05 | 0.36 | 0.05 | | | | C12 acid present (note 12) |
| ***L.*** *Amphora* 11.150.29 | | 0.04 | | 0.20 | 0.05 | 1.00 | 0.04 | 0.55 | 0.03 | 0.02 | 0.02 | | C12 acid present (note 13) |
| ***M.*** *Spouted dish* 10.176.47 | | trace | | 0.11 | 0.09 | 1.00 | | 0.30 | | | trace | | (See note 14) |
| ***N.*** *Pair of monkey jars* | | | | | | | | | | | | | |
| 10.176.49L | | trace | | 0.05 | | 1.00 | | 0.08 | | | 0.12 | | Beeswax, conifer resin (note 15) |
| 10.176.49R | | trace | | 0.08 | 0.02 | 1.00 | 0.01 | 0.18 | 0.02 | 0.03 | 0.09 | 0.03 | Beeswax, conifer resin (note 16) |
| ***O.*** *Duck flask (10)* 10.176.50 | | trace | | 0.04 | 0.01 | 1.00 | 0.03 | 1.50 | 0.01 | | | | (See note 17) |
| ***P.*** *Large monkey jar* 10.176.54 | | trace | | 0.33 | 0.11 | 1.00 | 0.04 | 0.33 | 0.03 | 0.03 | 0.04 | | Conifer resin (note 18) |

## NOTES TO TABLE 1

Specific objects are referred to in the text by the letter that precedes the name. The number in parentheses following the name corresponds to the catalogue in the accompanying paper by Biri Fay. Compounds whose relative abundances are shown are straight-chain fatty acids (identified by number of carbon atoms) and some dicarboxylic acids (identified by number of carbon atoms). The peak area of C16 (palmitic acid) is defined as 1.00 for all samples, and all other peak areas are relative to this. "Trace" indicates that a peak was present, but it was too small for reasonable quantification. If the box is empty, the compound was not detected. In the notes below, the range of straight-chain hydrocarbons, detected in many of the samples, is noted; "at similar abundances" means that odd-carbon number and even-carbon number hydrocarbons were equally abundant.

1. Methyl 7-oxodehydroabietate detected. Also detected: traces of odd- and even-number straight-chain hydrocarbons, at similar abundances; dimethyl o-phthalate (contaminant).

2. Methyl 7-oxodehydroabietate detected. Also detected: odd- and even-number hydrocarbons (C21–C33), odd-numbered ones much more abundant, maximizing at C27; C20, C22, C24 (most abundant), and C26 fatty acids.

3. Odd- and even-number hydrocarbons (C23–C31) detected (maximizing at C27, odd ones somewhat more abundant than even ones). Also detected: dimethyl o- and p-phthalates (contaminants). Two major peaks with retention times somewhat less than that of methyl palmitate were not identified (contaminants?).

4. Traces of hydrocarbons and dimethyl o-phthalate (contaminant) detected.

5. Methyl 7-oxodehydroabietate detected. Also detected: odd- and even-number hydrocarbons (C23–C30, odd ones more abundant, maximizing at C27).

6. Methyl 7-oxodehydroabietate detected. A phthalate (contaminant) was detected (tentatively identified as bis[2-ethylhexyl]phthalate).

7. Also detected: monounsaturated C18 fatty acids (abundance ~ 0.3 that of stearic acid).

8. Methyl dehydroabietate detected. Also detected: traces of odd- and even-number hydrocarbons (C22–C28), at similar abundances; dimethyl o-phthalate (contaminant). C12 (lauric) acid abundant (C12 acid/C16 acid = 0.19).

9. Odd- and even-number hydrocarbons detected (C21–C28), odd ones slightly more abundant, maximizing at ~ C22–C25. Also detected: dimethyl o-phthalate (contaminant).

10. Methyl 7-oxodehydroabietate detected. Also detected: odd- and even-number hydrocarbons in the range C19–C25, maximizing at C21. Also detected: dimethyl o-phthalate (contaminant). C12 (lauric) acid abundant (C12 acid/C16 acid = 0.26). Also detected: hydroxy- and oxo-fatty acids (not specifically identified).

11. Traces of hydrocarbons and dimethyl o-phthalate (contaminant) detected.

12. Odd- and even-number hydrocarbons detected (C19–C27), at similar abundances, maximizing at C21–C22. Also detected: dimethyl o-phthalate (contaminant); 9,10-anthraquinone. C12 (lauric) acid abundant (C12 acid/C16 acid = 0.49).

13. Odd- and even-number hydrocarbons detected (C21–C30), at similar abundances, maximizing ~ C22–C23. Also detected: dimethyl o-phthalate (contaminant). C12 (lauric) acid abundant (C12 acid/C16 acid = 0.13).

14. Odd- and even-number hydrocarbons (C22–C30, at similar abundances) detected. Also detected: dimethyl o- and p-phthalates (contaminants).

15. Methyl dehydroabietate and methyl 7-oxodehydroabietate detected. Also detected: odd- and even-number hydrocarbons (C22–C31), odd ones somewhat more abundant than even ones, maximizing at C27. Straight-chain alcohols (>C20) tentatively detected. Dimethyl p-phthalate and much lower amount of dimethyl o-phthalate (contaminants) detected.

16. Methyl sandaracopimarate, methyl dehydroabietate and methyl 7-oxodehydroabietate detected. Also detected: odd-number hydrocarbons (C22–C29), at similar abundances, maximizing at C27. Branched fatty acids detected, as well as, apparently, dicarboxylic acids (C24 and higher). Dimethyl o- and p-phthalates (contaminants) also present.

17. Odd- and even-number hydrocarbons detected (C22–C31), at similar abundances, maximizing ~ C27–C30. Also detected: dimethyl o-phthalate (contaminant).

18. Methyl dehydroabietate detected. Also detected: odd- and even-number hydrocarbons (C21–C29), odd ones slightly more abundant, maximizing at C25. Dimethyl o- and p-phthalates (contaminants) also detected.

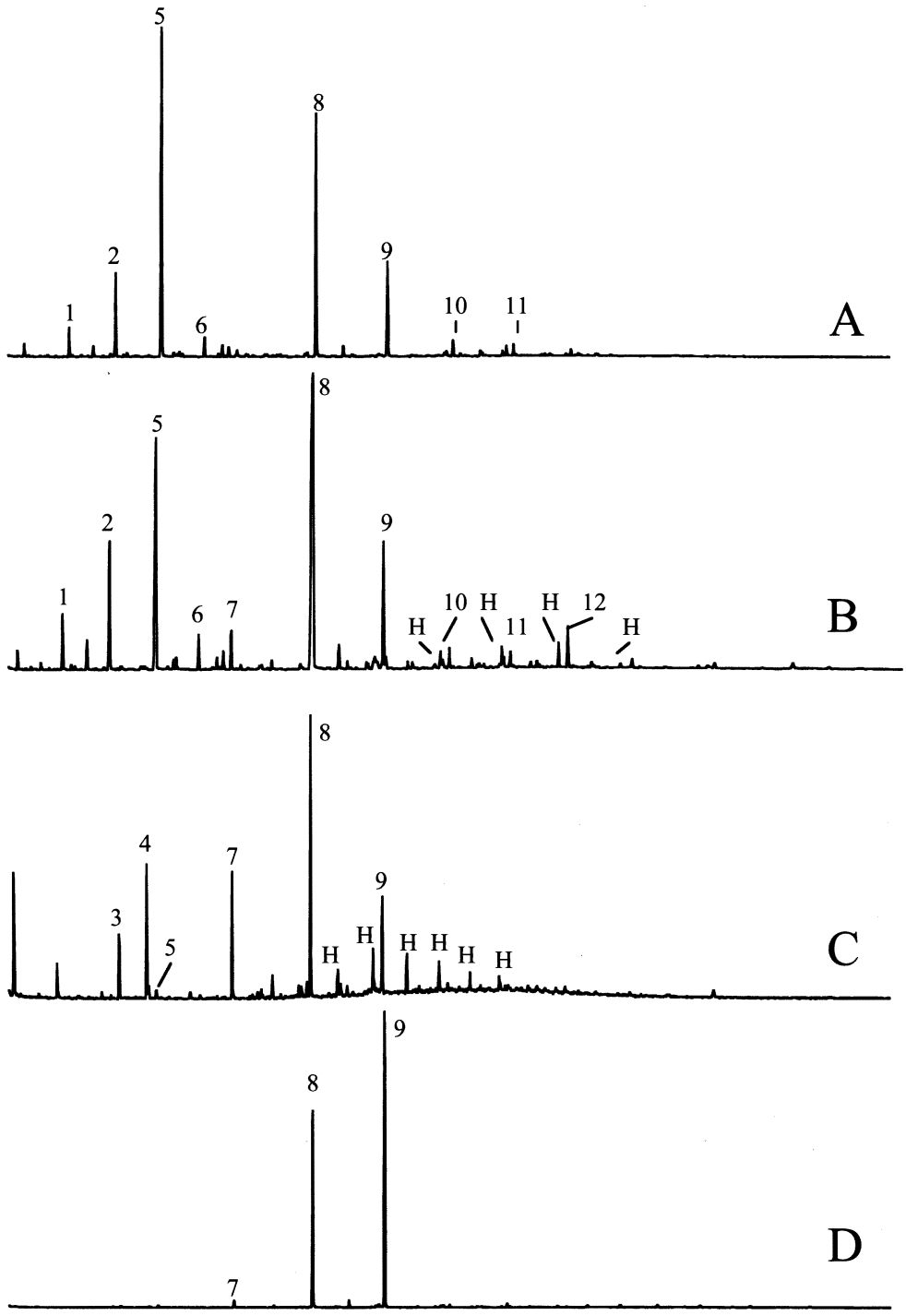


Figure 1. Total ion chromatograms of solvent extracts from four anhydrite vessels. Specific objects are identified by the letter references given in Table 1.(A) duck flask A; (B) vessel B; (C) bag-shaped jar K; (D) duck flask O. The horizontal axis is retention time (shown in each case is the region from 5 to 30 minutes). The vertical axis is abundance (total ion current); the scale for each chromatogram has been adjusted for ease of comparison. Some of the specific compounds in each chromatogram have been labeled. All acidic compounds were analyzed as methyl esters. Peaks 1, 2, 5, and 6 are dicarboxylic acids: 1, heptanedioic acid (diC7, pimelic acid); 2, octanedioic acid (diC8, suberic acid); 5, nonanedioic acid (diC9, azelaic acid); 6, decanedioic acid (diC10, sebacic acid). Peak 3 is o-phthalic acid, a contaminant. Peaks 4, 7–12 are straight-chain saturated fatty acids: 4, lauric (C12) acid; 7, myristic (C14) acid; 8, palmitic (C16) acid; 9, stearic (C18) acid; 10, eicosanoic acid (C20, arachidic acid); 11, docosanoic acid (C22, behenic acid); 12, tetracosanoic (C24) acid. Peaks labeled "H" are straight-chain hydrocarbons.

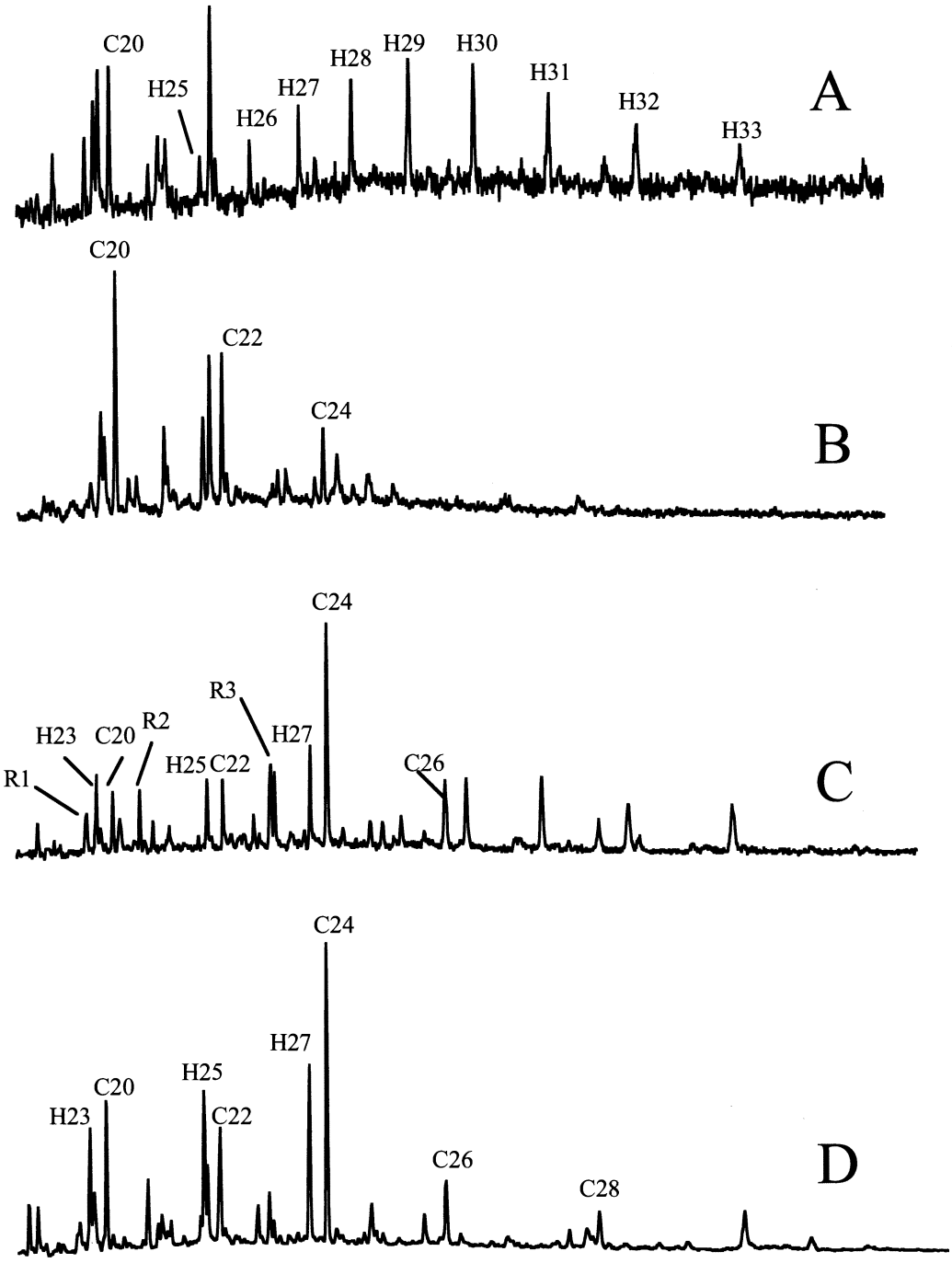


Figure 2. Details of total ion chromatograms of solvent extracts from four stone vessels. Specific objects are identified by the letter references given in Table 1. (A) duck flask O; (B) duck flask A; (C) pair of monkey jars N, sample R; (D) vessel B. The horizontal axis is retention time (16–30 minutes). The vertical axis is abundance (total ion current); the scale for each chromatogram has been adjusted for ease of comparison. Some of the specific compounds have been labeled. All acidic compounds were analyzed as methyl esters. Fatty acids are labeled with "C" followed by the number of carbon atoms in the specific compound. Straight-chain hydrocarbons are labeled with "H," again followed by the number of carbon atoms in the compound. Peak R1 is sandaracopimaric acid; R2, dehydroabietic acid; R3, 7-oxodehydroabietic acid.