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The mineral composition of dates

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THE MINERAL COMPOSITION OF DATES

Maurice Mortimer Cleveland

Thesis submitted for
the degree of
Master of Science

MASSACHUSETTS STATE COLLEGE, AMHERST

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I. INTRODUCTION

The chemical composition of the date is of interest because of the widespread use of this fruit as a human food. In the date-producing countries of the Orient and northern Africa it is a principal component of the diet. France and Italy import many dates from their colonies across the Mediterranean. In England the annual consumption is 3 pounds per capita. In Canada and the United States it is respectively, 1 pound and 0.43 pounds. The date industry in California and Arizona is important and is growing rapidly. The present production is over 3,000,000 pounds per year. The American grown dates, however, furnish only a small fraction of those consumed. Approximately 54,000,000 pounds of dates are imported annually, principally from Iraq at the head of the Persian Gulf.

While there are many varieties of dates, only a few are of commercial importance. The Deglet Noor is the principal American grown variety, while the Hallowi, Sayer, and Khadrawi comprise the greater part of the annual import. The present paper is concerned particularly with the more important imported varieties, Hallowi and Sayer. The specific purpose of the author in this investigation was to obtain exact information regarding the mineral constituents of these important varieties. A careful search of the literature revealed that

in the entire field covered by Chemical Abstracts, Chemischer Zentralblatt and the Experiment Station Record, only two mineral analyses of dates were reported, and these were on undescribed samples which may have been of either California or Iraq origin. In contrast, the literature contains numerous proximate analyses.

For the purpose of presenting a complete picture of the chemical composition of the date, a discussion of the organic composition, including vitamins, will be first given, followed by the mineral composition.

II. REVIEW OF LITERATURE

1. General Chemical Nature of the Date

The organic composition of the date is well known, due to the fact that it has received attention from three different groups of investigators: first, those interested in human nutrition; second, those interested in commercial artificial ripening; and third, those interested in plant physiology.

The date is outstandingly a saccharine fruit, 70 to 80 per cent of its dry weight consisting of sugar. On the basis of a number of analyses of Mesopotamian varieties, the date was at first believed to contain only invert sugar. It was later found that some African varieties contained cane sugar also. Slade (38) first pointed out that there are two distinct types of dates: the invert sugar type, possessing at maturity a large amount of invert sugar and little or no sucrose; and the cane sugar type, possessing at maturity practically all of its sugar in the form of sucrose. Vinson (45) showed that this difference was due to the lack of the enzyme invertase in the cane sugar type.

2. Relation of Composition to Stage of Maturity

Vinson (45) further demonstrated by means of analyses at different stages of maturity that nearly all of

the sugar of a date of the invert sugar type passes through the cane sugar stage and becomes inverted during ripening. In a later publication, (46) he presented evidence for the theory that the invertase of the unripe date is in an intracellular form, probably forming an insoluble compound with the protoplasm, and that during ripening the enzyme is changed into an extracellular form readily soluble in water. Associated with ripening also is the change of the soluble, astringent tannin into the insoluble, non-astringent form, in which it can be seen as brown granules in the ripe date. Lloyd (31) states that this loss of astringency is due to the union of tannin with an associated colloid of a carbohydrate nature. Vinson has published a bulletin (47) summarizing his several papers on the chemistry and ripening.

Several papers have also been contributed by Fattah on the chemistry and ripening. He states (21) that, in general, ripening involves a decrease in sucrose and tannin and an increase in reducing sugars. He and Cruess (22) further report that Mesopotamian dates show a higher percentage of sugar and a lower moisture content than California dates of the same variety, due presumably to more favorable climatic factors.

3. Proximate Analyses

The workers whose contributions have been reviewed above were interested primarily in the physiological process of ripening, with a view to artificially accomplishing this in un-

favorable climates, and were concerned only with sugar, moisture, and tannin contents. Another group, interested in human nutrition, has recorded more complete analyses, including the constituents usually considered to compose "proximate analyses," - moisture, N-free extract, protein (N.x 6.25), fat (ether extract), crude fiber, and ash, - and other constituents in some cases. More than a dozen such analyses are recorded in the literature. However, none of these complete analyses are described with respect to the variety of the sample. For purposes of uniformity in this paper, additional analyses were made in our laboratory of both Hallowi and Sayer varieties. These data are given in Table I. The samples were packaged dates, grown in Iraq in 1930 and packed by the Hills Brothers Company of New York.

Table I

Proximate Composition of the Edible Portion of Iraq Dates.

	Hallowi (percent)	Sayer (percent)
Moisture	19.0	18.0
Ash	2.22	1.59
Protein (N x 6.25)	1.72	2.16
Fat (Ether Extract)	1.90	0.31
Reducing sugars as invert	73.50	--
Total carbohydrates other than crude fiber	73.67	76.14
Crude fiber	2.17	1.90
Sucrose	None	--

The moisture content of bulk dates varies from 12 to 21 per cent, from 15 to 20 per cent being that of a palatable date. It may become considerably less in storage. As the date dries out, the dextrose crystallizes, probably as dextrose monohydrate, and the date becomes known to the trade as "sugared". Sugared dates are considered inferior both by the trade and by the public. However, they can be restored to a suitable moisture content by treatment with moist steam, as Clague and Fellers (15) have shown. Dates with a moisture content below twenty-three per cent will keep satisfactorily, because the high sugar concentration inhibits the growth of microorganisms (23).

The high percentage of sugar, approximately 75 per cent, gives the high calorific value of 1420 calories per pound (34). In this respect dates are practically on a par with figs and raisins, but higher than prunes.

The percentage of protein is low, approximately 2 per cent. In the date producing countries of the Orient and northern Africa the natives unknowingly compensate for this by the addition of milk to their diet of dates.

The percentage of fat is lower in the case of the analysis of the Sayer variety than it is in most of the reported analyses of undescribed samples of dates. (In this connection it is also interesting to note that whereas the percentage of "fat" by ether extraction was 0.31, duplicate

determinations with petroleum ether showed only 0.11 per cent.)

Sucrose, as the table indicates, is lacking in the Hallowi date. Both of the imported varieties, Hallowi and Sayer, are of the invert sugar type, while the principal American grown variety, the Deglet Noor, is of the cane sugar type.

The percentage of ash is high and is comparable to that of other dried fruits.

4. Ratio of Edible Portion to pit

The ratio of edible portion to pit is variable in different varieties of dates, but at a definite moisture content is relatively constant for a given variety. Table II gives the percentage of edible portion and pit of those samples which were later used for mineral analysis. In separating the edible portion from the pit, care was exercised to secure as good a separation as possible, but the pits were not cleaned. This was considered to be comparable to the separation which a consumer would make in eating unpitted dates and ejecting the stones from the mouth.

(See Table II)

5. Gums and Pectin

The available information on the gums and pectin in dates is very meager. Grimbert (25) mentions that gums

Table II.

Percentage of Pit and Edible Portion*

Description of Sample	% pit	% Edible Portion	% Moisture in Edible Portion	% Edible Portion at 16% Moisture**
Hallowi, 1928 crop	13.4	86.6	14.8	86.8
" " "	13.4	86.6	16.0	86.6
" 1929 "	12.1	87.9	12.2	88.4
" 1930 "	12.9	87.1	11.75	87.6
Sayer, 1929 "	10.3	89.7	13.6	90.0
" , 1930 "	10.3	89.7	12.3	90.1

* Determined on samples of 100 dates each

** Calculated from the accompanying data, on the assumption that all of the additional moisture would be contained in the edible portion.

and pectinous materials are present, while Vinson (47) states that "pectin bodies are often present in considerable amounts and cause the juice to jelly on long boiling. Such jelly, prepared by the native Mexicans is known as colache." No quantitative data appears in the literature.

The author carried out a determination of alcohol precipitate, commonly referred to as "pectin", according to the method of the Association of Official Agricultural Chemists (2) for fruits and fruit products, on a sample of Sayer dates and found them to contain 0.43 per cent "pectin" on a moist basis. The moisture content was 13.6 per cent.

The author also made a qualitative examination of the gum of Sayer dates, using the qualitative tests given by Jacobs and Jaffe (27) in their method for the identification of common gums. Their method of separation of the gums prior to identification tests, however, did not take into consideration the possible presence of pectin in the material for analyses. It therefore became necessary to modify their method by introducing a procedure from an earlier paper by Cook and Woodman (16) for the removal of pectin.

It was not surprising to find that the date gum could not be positively identified with any one of the common gums included in the Jacobs and Jaffe identification schema. However, it appeared to resemble gum arabic in several of its reactions.

6. Vitamin Content

Dates are a good source of certain of the vitamins.

M. C. Smith and Meeker (40) have shown in a study of three Arizona varieties, the Deglet Noor, the Maktum and the Thoory, that they are a good source of vitamins A and B (complex), but that they contain no appreciable C, D, or G. McLeod and Booher (32), however, have reported that the dried date does contain some vitamin C, but is a poor source of this factor. A definite antiscorbutic value was not obtained by them because of the refusal of the animals to eat the dates over an extended period of time. Chan (14) reports that fresh Chinese dates contain appreciable amounts of vitamin C.

S. L. Smith (41), referring to a preliminary report of the work of M. C. Smith and Meeker mentioned above, has rated dates as "vitamin A (+)" and "vitamin B (++)" on a scale giving a maximum of (+++) to any food material. Weston and Levine (44), have classed dates with the "good" sources of vitamin B₂. Sherman and Smith (37) state that dates fall in that class of fresh vegetables and fruits which contain from one to ten units of vitamin A per gram. Banana, dried prune, raw and canned tomatoes, considered good sources, are in this group.

III. EXPERIMENTAL PART

1. Analytical Methods

a. Sampling

The objective in sampling was to obtain a representative, composite sample large enough so that all of the proposed mineral determinations could be made upon portions withdrawn, and calculated to a common basis of moisture and ash content.

The first plan for securing such a representative sample was to accumulate a considerable quantity of ash, which could be well mixed, and weighed out in suitable portions. This proved impracticable, however, as no method could be devised whereby more than about 20 grams of dates could be satisfactorily ashed in one portion. In the case of larger amounts, the heat developed within the mass from its own combustion was great enough to cause slight fusion, inclusion of carbon, and probable volatilization of alkali chlorides.

Preliminary charring, grinding, and mixing of a considerable quantity of dates was also tried as a method of sampling, but it was found that even a small portion of this compact charred powder did not ash well.

The method finally adopted was to grind four times through a meat grinder a composite of 100 dates. The dates

comprising this sample were selected from a larger composite consisting of handfuls of dates from various parts of a 72 pound case. The desired number of clean whole dates was selected. These dates were then pitted carefully, so that a minimal amount of edible portion should cling to the pit. The edible portions were then ground through a well-tinned meat chopper. Although the precaution was probably unnecessary with a material of this comparatively non-acid nature, the first date through the chopper was discarded for the purpose of avoiding iron contamination. After the passage of one date, the grinding surfaces remained covered with a sticky, protective coating.

The ground, composite sample was then placed in a vacuum-seal quart jar, of the type used in canning, and was allowed to stand for two days, tightly covered, until presumably the moisture content had become uniform throughout the mass. Portions were then weighed out as needed for the determinations of moisture, ash, etc. These withdrawals were made as rapidly as possible, to avoid loss of moisture. When not in use the jars were kept tightly sealed in a cool place.

b. Determination of Moisture

It was necessary to determine the moisture of the composite samples in order that, for purposes of comparison,

the percentages of mineral constituents in different samples could be calculated on a dry basis.

For this purpose the toluene distillation method of Bidwell and Sterling (12) was first tried. This method gives a rapid and accurate determination in the case of substances to which it is adapted. However, in the case of biologic material containing sugar an error is introduced, because of the slow caramelization of sugar at the temperature of boiling toluene (110° C.) with the production of free water. In the case of dates of the invert sugar type this error is particularly serious, due to the large proportion of levulose, which decomposes appreciably at temperatures over 70° C. Nevertheless, the method has been applied with success to dates by G. H. Needham of the Hills Brothers Company, who continues the distillation empirically for a time period which has been found to give good correlation with moisture results obtained by the vacuum drying method.

It was thought that the same empirical procedure could be applied to dates in the present case. However, the ground, composite sample formed a sticky, solid mass which could not be broken up into small particles without loss both of moisture from its fresh macerated surface and of actual particles of sample. The material was unavoidably in large lumps, and the conditions of the distillation were consequently quite different from those for which the

empirical procedure had been worked out. The method was therefore abandoned.

The method of the Association of Official Agricultural Chemists (3) for fruits and fruit products was then adopted, with some necessary modifications. The vacuum oven available was not heated by an electrical unit capable of accurate control, but by a jacket of water heated by bubbling steam, and subject to variation in temperature with variation in pressure in the steam line. Therefore, in order to insure against accidental overheating and consequent decomposition of the easily destructible levulose, it was decided to run the apparatus at a level lower than the 70° C. recommended by the Association of Official Agricultural Chemists, and to continue the desiccation until the samples attained constant weight. An attempt was made to hold the temperature at about 50° C., but fluctuations occurred within the range of 40 to 60° C. The vacuum was easily maintained at a pressure well under the 100 mm. limit recommended in the method.

The time required for desiccation to constant weight was surprisingly long. In the first set of determinations, the samples were weighed every day for 10 days before constant weight was attained. At the end of this period they were light colored and had no odor of caramelization. Subsequent sets of determinations were desiccated without interruption

for seven days, then weighed, replaced, and weighed again on the eighth day. No loss was found after the seven day period.

An illustration of the errors which may arise when temperatures higher than 70°C . are used was furnished by four samples which were overheated by an unexpected rise in the steam pressure. These samples reached 85°C . during one night, but were otherwise treated in the manner described above. Upon opening the oven a burned odor could be detected, and the samples appeared darkened. The moisture content in this determination averaged 0.7 per cent higher than in a subsequent determination in which proper conditions were observed.

c. Determination of Total Ash

The determination of the percentage of ash was found to be difficult. The prime objective is the complete combustion of organic matter without loss, either mechanically or by volatilization, of any of the mineral matter. This must be accomplished without the addition of any substance to aid combustion or to "fix" the more volatile ash constituents, the alkali chlorides.

The use of nitric acid or sulfuric acid, respectively, for these purposes changes the composition and the weight of the ash by replacing the natural carbonates and chlorides with the heavier nitrate and sulphate radicals.

Careful ashing at low temperatures alone must be relied upon. Table III is illustrative of the variations in results which may occur with the use of temperatures no more accurately defined or controlled than the "dull red heat" ordinarily recommended. It also, in connection with the subsequent discussion, brings out the importance of carrying on duplicate determinations of ash separately rather than simultaneously if any indication of the correctness of the results is to be obtained. (See Table III)

The "parallel triplicates" of the table were treated as follows: Approximately 20 grams of the composite sample was weighed in two or three pieces into each of three porcelain evaporating dishes. These samples were first charred in an oven over a gas stove, after which the dishes were placed on tripods over Bunsen burners and heated gently. The bottoms of the dishes became faintly red, and the charred samples began to glow at the edges. A gentle heat was maintained for one to two hours, while combustion spread throughout the mass. When the glow had died down the dishes were placed in a muffle at a faint red heat for two hours.

As the table indicates, this procedure gave three checks which appeared to be satisfactory for material of this nature. A slight amount of carbon remained, which was not driven off by a subsequent ignition at a somewhat stronger red heat.

Table III

Variation in Apparent Percentage of Ash in Dates
with Variation in Method of Ashing.

Conditions of Ashing	Per Cent Ash in Samples (Moist Basis)					
	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
Parallel Triplicates					1.64 1.63 1.64	
Parallel Duplicates			1.55 1.56	1.75 1.77		1.67 1.68
Parallel Duplicates			1.57 1.54	1.77 1.80	1.58 1.56	1.64 1.65
Non-Parallel Individual Determinations (Improved Technique)	2.03 2.05 2.03	2.12 2.10 2.11	1.68 1.65 1.67	1.89 1.88 .	1.67 1.67 1.66 1.68	1.71 1.71 1.72 1.72

However, subsequent "parallel duplicates", treated as the triplicates had been, while yielding satisfactory checks in themselves, showed that different pairs of duplicates on the same sample varied as much as .07 per cent in the percentage of ash obtained.

In order to determine whether or not this variation could be due to variations in the weight of the small carbon residues mentioned above, 12 samples were dissolved in dilute hydrochloric acid, and the solutions filtered through ignited

Gooch crucibles. The crucibles were then dried at 110°C . for two hours, weighed, ignited at a moderate red heat, and weighed again.

It was found that if the entire loss of weight arrived at in this manner was assumed to be due to carbon, the carbon present would make the result only 0.01 to 0.02 per cent of ash too great, and would cause a variation between duplicates of not over 0.01 of a per cent. From this it appeared that the variation must be principally due to variable volatilization of ash constituents.

With this in mind, further determinations were made in the following manner:

A sample of approximately 16 grams was weighed out in two or three thin strips covering the bottom of a platinum evaporating dish. It was placed in a cold muffle furnace, and slowly charred and ashed at a temperature below any redness during a period of 8 to 12 hours. Duplicates were not ashed simultaneously.

The results obtained by this method are given in the table as "non-parallel individual determinations." It will be seen that good agreement was obtained, and that all results were higher than those previously found. The ash itself was nearly white, with much less carbon than before and with no signs whatever of fusion. It is felt that these results are very near to the true values.

d. Determination of SiO_2 , P_2O_5 , Fe_2O_3 ,
 Al_2O_3 , CaO , MgO , Mn_3O_4

The method used for the determination of these elements was, in general, the gravimetric separation outlined by the Association of Official Agricultural Chemists (4) for determining these constituents in plant materials. Several modifications were made.

The method is subject to the criticism that it is long and cumbersome, especially in that it involves in the latter part of the process the removal of the molybdate added in the earlier part, and the destruction of large amounts of ammonium salts which have accumulated. Both of these steps are troublesome and time-consuming.

The method was adopted, nevertheless, because it was recognized as an official method among agricultural chemists. However, it has since been deleted by vote of the Association from the 1930 edition of "Methods of Analysis." The procedure for the determination of silica is the only portion which remains. The new edition substitutes other methods in which each of the constituents is determined on a separate aliquot of the ash solution, rather than by consecutive separation from one original solution.

The modifications introduced by the author will be noted in the order in which they are encountered in the procedure. The first modification was that sand was not

separated from soluble silica, but the two were ignited and weighed together and reported as SiO_2 .

The second modification was the introduction into the process of a determination of phosphate at the point at which the phosphate has been removed from the solution as ammonium phosphomolybdate, preparatory to precipitating iron and aluminum with ammonia. The phosphate was reprecipitated and determined as magnesium pyrophosphate, using the conditions of precipitation recommended by Epperson (18). These conditions were selected by the author because previous experience with Epperson's method had invariably shown it to yield a magnesium ammonium phosphate precipitate of the desired characteristics. In view of the data presented by Fales (19) on the solubility of magnesium ammonium phosphate hexahydrate, sufficient ammonia was added before the digestion period to make the solution 1.5 molar in this respect, instead of adding the lesser amount suggested by Epperson. It is recognized by the author that the phosphorus thus determined in the ash without special ashing methods does not necessarily include all of the phosphorus in the original material; but it seems probable that the discrepancy would not be significant in a material of this nature, which yields an alkaline ash.

The third modification was a slight one in the precipitation with ammonium hydroxide. In view of the fact that aluminum hydroxide is soluble in a slight excess of the

reagent, the instructions to "neutralize with dilute ammonium hydroxide (1 + 4); add about 1 cc. excess of the reagent" were followed very carefully. It was found, however, that if after filtration two or three cubic centimeters of the reagent were added to the clear filtrate, and the solution allowed to stand for two or three hours at a temperature of 30°-40°C., a further slight precipitation of aluminum occurred. Accordingly an initial addition of four cubic centimeters, instead of one, of excess reagent was practiced with satisfactory results. At no time later in the process did any aluminum appear in neutral solutions to indicate that too great an excess of ammonia had initially been added.

The fourth modification was made in the washing of the ammonia precipitate. Hillebrand and Lundell (26), state that hot water cannot be used in washing this precipitate, for aluminum hydroxide readily assumes the colloidal state. This was found to be true. In the later stages of the washing, when the salts had been largely removed, colloidal aluminum hydroxide began to come through the filter. Accordingly the suggestion of these authors that a two per cent solution of ammonium chloride (two grams in 100 cubic centimeters of solution) be used for this washing was adopted.

The fifth modification was the use of the Jones reductor for reducing the iron preliminary to its titration with permanganate. This was regarded as having the advantages that the necessity of filtering out and washing an excess of zinc was avoided, and that any iron contamination which might be introduced in the reduction could be readily deducted after carrying out an easily performed blank determination. The conditions recommended by Fales (20), were observed. (Iron was also determined colorimetrically to verify the results obtained by this method. The colorimetric method will be discussed later.)

The sixth modification was made in the process of expelling ammonium salts and removing molybdic acid, prior to the determinations of manganese and magnesium. These operations were both very troublesome. At first the ammonium salts were expelled in the manner directed, simply by evaporating the solution to dryness and then heating the dish from above until no more white fumes were given off. There was appreciable spattering in the heating process despite the exercise of extreme care. This was due to a large amount of ammonium nitrate which had been introduced into the solution with the ammonium molybdate and in the washing of the ammonium phosphomolybdate precipitate. Ammonium nitrate melts before decomposing and the result upon heating the salt was

a heavy bubbling liquid. Complete decomposition was finally accomplished, but some spattering had occurred. Furthermore, a strong heat was required to drive off the last traces of the ammonium nitrate. This heat apparently had also the effect of decomposing most of the molybdic acid to molybdic oxide, which is soluble in acid. Consequently, when hydrochloric acid was added to the residue for the purpose of dissolving the desired constituents, the oxide also was dissolved, leaving only a very small residue of molybdic acid for removal by filtration. Fortunately it was found that boiling the solution would hydrate the molybdic oxide, to form molybdic acid again, which could then be filtered off.

It was thought that the spattering could be avoided, and that possibly the objectionably high finishing temperature with its undesirable effects could be obviated if the ammonium nitrate was converted into ammonium chloride. This decomposes directly without melting. In order to bring this about, the solution was evaporated with hydrochloric acid as before; but the subsequent heating to expel the salts was carried only to the point at which ammonium chloride ceased to come off freely, and at which the ammonium nitrate began to bubble. The dish was then allowed to cool; dilute hydrochloric acid was added; and that portion of the molybdic acid which had

become insoluble was filtered off. Strong hydrochloric was then added to the filtrate, and the solution was again evaporated to dryness. This was repeated several times. Heating to expel the ammonium salts was then resumed, and carried to completion, without the occurrence of spattering or the necessity of heating strongly in order to drive off the last traces.

This modification was successful as far as avoiding the mechanical loss of spattering was concerned, but the molybdenum was left again in a form soluble in water, and soluble to some extent in dilute hydrochloric acid. This form of molybdenum was of a light blue color. (Evidently in the absence of nitrates at least a part of the molybdic acid had been reduced to molybdenum blue.) By the time that the molybdenum residue remaining after the addition of dilute hydrochloric acid and subsequent filtration had been thoroughly washed with water it had practically all dissolved and re-precipitated in the acid solution below. This suspension was evaporated to dryness and taken up in stronger hydrochloric acid (1 + 3). This time the residue after filtration was washed with acid of the same strength, instead of with water. A portion of the residue remained undissolved after the washing. Some advance was thus made, but a large part of the molybdenum was still in solution. The solution was once more

evaporated to dryness.

In view of the well-known colloidal properties of molybdenum blue it was decided to take up the residue this time with a few cubic centimeters of strong hydrochloric acid as directed in the method, and to try washing the insoluble residue with one per cent salt solution. This was successful. Practically all of the molybdenum remained insoluble on the filter paper.

The seventh modification used by the author has been previously mentioned in discussing the second one. In short, the method and conditions of Epperson (18) were again used in the precipitation of magnesium ammonium phosphate hexahydrate, this time in determination of magnesium at the end of the long separation.

e. Determination of Sodium and Potassium

The method used for the determination of sodium and potassium was that of the Association of Official Agricultural Chemists (5) for plants. The only modification of the given procedure introduced was that the precautions previously discussed with respect to the precipitation and washing of aluminum hydroxide were observed.

f. Determination of Sulphur

The method used for the determination of sulphur in ash was that of the Association of Official Agricultural

Chemists (6) for fruits and fruit products. It is to be noted that the amount of sulphate in the ash does not necessarily represent all of the sulphur in the original material. Special ashing methods must be used if total sulfur is desired.

g. Determination of Chlorine

Chlorine was determined by the method of the Association of Official Agricultural Chemists (7) for fruits and fruit products.

h. Determination of Iron (Colorimetric)

Particular interest attaches to the percentage of iron because of the significance of this element in nutrition. For this reason it was desired to verify the results obtained by the gravimetric method of the Association of Official Agricultural Chemists, by means of a direct determination which would eliminate the possibility of contamination from reagents. For the determination of very small amounts of iron, colorimetric methods are most suitable. Stugart (43) in a recent paper has given an excellent discussion of the existing methods for the determination of iron in biological materials. His modification of the thiocyanate method was used by the author. Extreme care was taken to avoid contamination with iron in any way.

A comparison of the results obtained by this method with those previously obtained by the gravimetric method is of interest. The percentage of iron in ash obtained colorimetrically was lower than that obtained in the gravimetric separation. This was to be expected, since three of the reagents used in the former determination contained traces of iron. The hydrochloric acid contained, according to the label analysis, not over 0.00005 per cent; the nitric acid, not over 0.0002 per cent; the pyrosulphate, not over 0.00006 per cent. These reagents were used in somewhat indeterminate amounts. However, a rough calculation, based on the assumption that they contained the maximum amounts of iron allowed by the labels, indicated that in four samples an average amount of Fe_2O_3 equivalent to 0.063 per cent of the ash had been added. The average of results obtained by the colorimetric method was 0.06 per cent lower than the average of those obtained by the original gravimetric method. This correlation seems a good verification of the correctness of the data, although it is based on the label analyses, which were not verified.

1. Determination of Copper

The recently discovered physiological importance of copper has also turned especial interest toward the

development of methods for determining accurately the occurrence of very small amounts of this element in biological material. The most recent contribution to this subject is that of Ansbacher, Remington and Culp (1). Their method was used by the author. Extreme care was used to prevent any contamination with copper, and all reagents were tested for its presence. The distilled water was redistilled in glass apparatus before use. Some modifications in technique were introduced, which were thought to lessen the danger of contamination. The wet-ashing alternative was used in preparing the samples.

j. Determination of Boric Acid

Boric acid was determined by the Gooch method, as described by Leach (28).

k. Determination of Alkalinity

The method used for the determination of alkalinity was that of the Association of Official Agricultural Chemists (8) for fruits and fruit products.

2. General Composition of the Ash

The percentage composition of the ash of Iraq dates of the Hallowi and Sayer varieties, as determined by the author, is shown in Table IV. Each column of data is

the analysis of a sample representing a 72-pound case of bulk dates of the variety and crop designated. The determination of each element except copper was made in duplicate, and the determinations of percentage of ash and of SO_3 were made in triplicate. (See Table IV)

The first point to be noted in the table is the percentage of ash in the dry date, approximately 2 per cent. This is two or three times as high as that of most of our foods which yield an alkaline ash. Most fresh fruits and many vegetables have less than 1 per cent of ash. Other dried fruits, such as prunes and raisins, have a percentage of ash which is comparable to that of the date. However, in consideration of the manner of their use in the dietary, dates can more fairly be compared with fresh fruits than with dried ones.

The second point to be noted is the large proportion of potash in the ash. This is an important factor in the high alkalinity, which will be discussed later.

Other constituents of particular interest are iron, manganese, and copper. These also will be discussed later in connection with the work of other analysts.

Table V presents for comparison the only mineral analyses of dates reported in the literature, and the averages of the author's analyses of the Hallowi and Sayer varieties.

The analyses are in good agreement, except in a few particulars. The percentage of Na_2O obtained by Forbes,

Table IV.
 Percentate Composition of the
 Ash of Iraq Dates

Variety	Hallowi				Sayer	
	1928A	1928B	1929	1930	1929	1930
Crop						
Ash content, dry dates, per cent	2.40	2.51	1.90	2.14	1.93	1.95
K ₂ O	46.9	46.0	42.2	43.2	41.2	40.5
Na ₂ O	2.02	2.65	2.80	2.15	2.55	2.76
CaO	4.35	3.88	4.75	4.27	6.34	7.58
MgO	5.31	5.45	6.34	5.38	6.64	6.90
SiO ₂	5.81	7.40	7.01	7.03	7.80	6.69
Fe ₂ O ₃	0.21	0.23	0.32	0.20	0.27	0.19
Mn ₃ O ₄	0.20	0.15	0.25	0.21	0.26	0.40
Cl	16.90	18.16	12.01	14.65	15.46	17.83
SO ₃	6.19	6.33	6.99	5.91	7.26	7.90
P ₂ O ₅	7.89	7.38	10.12	8.88	8.13	6.81
CuO			0.017	0.012	0.013	0.015
Al ₂ O ₃	0.50	0.46				

Table V.

Percentage Composition of the Ash of
Dates
(Compiled from different sources)

Source of Data	Benoy (9)	Forbes, Beagle Mensching (24)	This Investigation	
Variety	(not stated)	(not stated)	Hallowi	Sayer
No. of Samples	1	1	4	2
Ash content, dry dates, per cent	2.04	1.92	2.24	1.94
K ₂ O	45.04	41.8	44.6	40.8
Na ₂ O	2.36	8.08	2.41	2.65
CaO	6.63	6.12	4.31	6.96
MgO	6.52	7.42	5.62	6.77
SiO ₂	5.77		6.81	7.24
Fe ₂ O ₃	0.47		0.24	0.23
Mn ₃ O ₄			0.20	0.33
Cl	19.06	14.85	15.43	16.64
SO ₃	7.35	11.32	6.36	7.62
P ₂ O ₅	0.78	9.18	8.57	7.47
CuO			0.015*	0.014
Al ₂ O ₃			0.48 *	

* Two samples only

Beagle, and Mensching (24) is distinctly higher than that obtained by either Benoy (9) or in this investigation. This may be due to the fact that Forbes and his coworkers used an original method for determining the total of sodium and potassium, while both Benoy and the author used the method of the Association of Official Agricultural Chemists (5). In each case sodium itself was determined by difference, from the result for total sodium plus potassium, the latter being determined directly by the chloroplatinate method.

The result for percentage of SO_3 obtained by Forbes and his coworkers is also higher than that obtained by either Benoy or in this investigation, although perhaps not beyond the range of biological variation. It represents total sulfur in the material, however, while the results of of this research are on sulfur in ash. It seems unlikely that this fact would account for the difference, in the case of a material of alkaline ash and of such a low protein and fat content. Whether Benoy's value represents total sulfur or sulfur in ash is not stated.

Another distinct difference is found between the percentages of phosphorus reported by Benoy, and those reported by both Forbes and his coworkers and this investigation. This seems to be more than a normal variation. No explanation other than a possible error in decimal point can be suggested.

3. Content of Iron, Copper and Manganese.

Table VI presents all of the data on the iron content of dates which is to be found in the literature, together with the data obtained in this investigation.

(See Table VI)

The iron is reported on a moist basis, since some of the data in the original articles were presented on a moist, or "as purchased", basis without information as to the moisture content. Where information on this point was given it is included in the table.

The data show the variation characteristic of biologic material, but all are in the same general range. Stiebeling (42) has compiled a table of the iron contents of fresh fruits and vegetables, and from this compilation has made an arbitrary classification of 98 of them as poor, fair, good, and excellent. Those containing over 0.0016 per cent of iron, she considers "excellent." Spinach, chard, dandelion greens, and lima beans are examples of this class. It is evident that dates are in the class with these materials. However, it must be remembered that dates are much lower in moisture content and would appear less favorably if comparisons were made on a dry basis.

Table VII presents the only reports on the copper and manganese content of dates which are to be found in the literature, together with the data obtained in this investigation.

(see Table VII)

Table VI.

Iron Content of the Edible Portion of Dates
(Moist basis)

Source of Data	Description of Sample	% Fe	% Moisture
Sherman	(35) -	.003	-
Petersen and Elvehjem	(33) -	.00507	27.5
Benoy	(9) "standard brand on market"	.0049	28.4
Stiebeling	(12) { Iraq packaged dates	.00394	-
	{ " " "	.00302	-
	{ " " "	.00399	-
Bunge	(13) -	.0018	-
This Investigation	{ Iraq bulk dates, Hallowi	.0030	14.8
	{ " " " "	.0034	16.0
	{ " " " "	.0037	12.2
	{ " " " "	.0026	11.8
	{ " " " Sayer	.0032	13.6
	{ " " " "	.0023	12.3

Table VII
Copper and Manganese Content of the Edible
Portion of Dates
(Dry basis)

Source of Data	Description of Sample	% Cu	% Mn
Lindow, Elvehjem, Petersen (30)	-	.00053	
Lindow and Petersen (29)	-		.00019
This Investigation	(Iraq bulk dates, Hallowi	.00026	.0035
	" " " "	.00021	.0027
	" " " "		.0034
	" " " "		.0032
	" " " Sayer	.00020	.0036
	" " " "	.00023	.0056

The amount of copper found is lower than that found by Lindow, Elvehjem, and Petersen (30), but in the same general range. These authors have determined the copper content of 160 different food materials, and have classified them, in descending order of copper content, on a fresh basis, as follows: nuts, dried legumes, cereals, dried fruits, poultry,

fish, animal tissues, green legumes, roots, etc., leafy vegetables, fresh fruits, and non-leafy vegetables. The data obtained by the author would on this moist basis of comparison drop dates below the average of dried fruits down to the class average of fish.

There is a distinct difference between the percentage of manganese obtained by Lindow and Petersen (29) and that obtained in the present investigation. This difference is difficult to explain. While it is true that Lindow and Petersen analysed only one sample of dates, in contrast to the author's six samples, they have the supporting evidence that other dried fruits which they analysed fell in the same range. The uniformly higher results of the author on six samples from the same locality could be due to the nature of the soil.

The analytical method used by Lindow and Elvehjem was undoubtedly better than that used by the author. It was direct, whereas the author's method separated manganese in the course of a long gravimetric determination which included first the determination of several other constituents. No manganese was shown in the label analyses of the reagents used, but its entire absence was not verified. However, as has been shown, the amount of iron added in the reagents was slight, and it seems very unlikely that manganese contamination, which was not even mentioned on the labels, could be three or four times greater than the iron contamination.

The author believes that the large amount of manganese reported is not due to any contamination with other elements in the precipitate weighed. A study of the method, in connection with incidental observations in the course of the determination, makes it seem certain that the precipitate could not have been contaminated with silica, iron, or aluminum.

4. Content of Boric Acid and Zinc

The available data on the boric acid content of dates is shown in Table VIII.

Table VIII

Boric Acid Content of the Edible Portion of Dates (Moist basis)

Source of Data	Description of Sample	% H_3BO_3
Smith, A. H.	(39) -	.03
Dodd	(17) Persian dates	.006
This Investigation	Iraq dates, Sayer variety, 1930	.037

Smith (39) made determinations on six dried fruits and found them to contain from 0.002 per cent to 0.008 per cent of boric acid with the exception of the date, which contained 0.03 per cent. The author's value agrees well with

that obtained by Smith. Dodd (17) has analysed about 50 fruits and vegetables, and has found them to contain from 0.0 per cent to 0.025 per cent. Each analyst has employed a different method.

Zinc has been determined in a large number of fruits and vegetables by Bertrand and Henson (10). Dates were found to contain 3.4 mg. per kilo of fresh material; 4.3 mg. per kilo on a dry basis; and 94 mg. per kilo of ash (11). Compared on the basis of fresh material they have a higher zinc content than any of the fruits listed. These include oranges, lemons, peaches, plums, apricots, strawberries, bananas, and tomatoes. They fall in the class with turnips and asparagus.

5. Alkalinity of the Ash

The alkalinity of the ash is given in Table IX.

The data presented from Benoy (9), and from Forbes, Beegle and Mensching, (24) was calculated by the author from the mineral analyses given by them. None of the data from any of the analysts differs significantly from the general trend. The titration data of the author presents the averages of triplicate determinations.

The alkalinity, as calculated on a dry basis, is not high in comparison with other fruits and vegetables. However, when a comparison is made on the "as purchased" basis the

Table IX.
Potential Alkalinity of Dates *

Source of Data	Description of Sample	Alkalinity calculated from analysis**	Alkalinity determined by titration
Sherman*** (36)	-	13.8	
Benoy (9)	"standard brand on market"	17.6	
Forbes, Beagle, Mensching (24)	-	17.5	
This Investigation	(Iraq bulk dates, Hallowi, 1928	17.7	17.0
	{ " " " " 1928	17.5	16.9
	{ " " " " 1929	15.7	16.65
	{ " " " " 1930	15.5	16.7
	{ " " " Sayer 1929	15.1	16.3
	{ " " " " 1930	15.2	15.5

* Excess of base-forming over acid-forming constituents in the ash from 100 grams dry material, expressed as cubic centimeters of normal alkali.

** Only K_2O , Na_2O , MgO , CaO , Cl , P_2O_5 , and SO_3 were considered.

*** The value given in the reference is on a moist basis. The value here given is calculated on the assumption of a 20% moisture content.

date becomes one of the best of the "potential alkalinity" sources. Data from Sherman(36) is presented in Table X to illustrate this point. (See Table X)

The value given for dates in this table is the average of the author's results on six samples. The whole table is based on the alkalinity calculated from mineral analyses rather than on values obtained by the titration method.

Table X
Potential Alkalinity of Foods

Food	Alkalinity of ash in terms of cc. of normal alkali per 100 grams of edible portion.
Spinach	27.0
Raisins	23.7
Dried Beans - - - - -	18.0
Dates	13.9
Carrots	10.8
Lettuce - - - - -	7.4
Potatoes	7.
Tomatoes	5.6
Oranges - - - - -	5.6
Lemons	5.5
Grape juice	3.9
Apples - - - - -	3.7
White bread	acid
Meat	acid

IV. SUMMARY

Complete mineral analyses of six samples of dates, covering two varieties and three crop seasons, were made. No marked differences were observed in the amount or composition of ash in the crops from different seasons. This was true of both Hallowi and Sayer varieties. Similarly there were no striking differences between these two varieties. The percentage of ash is high. On a moisture-free basis it varied from 1.9 to 2.5 per cent. The outstanding characteristic of the ash was the high proportion of potash, which comprised from 40 to 47 per cent of the total. Other principal base-forming constituents were: CaO , 4 to 8 per cent; MgO , 5 to 7 per cent; and Na_2O , 2.0 to 2.8 per cent. The principal acid-forming constituents were: Cl , 12 to 18 per cent of the ash; P_2O_5 , 7 to 10 per cent; and SO_3 , 6 to 8 per cent.

The iron content of the date was found to be high for a plant material, comprising 0.0025 to 0.0037 per cent of the "as purchased" edible portion. On the same basis the copper content was fairly high, 0.0002 to 0.0003 per cent, and manganese was found to the extent of 0.003 per cent.

Boric acid was present as 0.04 per cent of the edible portion.

High alkalinity was another outstanding characteristic of the date ash. The ash from 100 grams of dry material was equivalent to 15 to 17 cubic centimeters of normal alkali.

Pectin (alcohol precipitate) was present to the extent of 0.43 per cent in a sample of Sayer dates.

Qualitative examination of the gum from Sayer dates showed that it resembled gum arabic in some of its reactions. The exact nature of the gum was not determined.

The proportion of edible portion to pit is a variety characteristic. The Hallowi pits constituted 13 per cent of the total weight of the date, compared with 10 per cent for the Sayer.

The large proportion and well-balanced distribution of the minerals, and the high sugar content, make the date a valuable adjunct to the diet.

V. BIBLIOGRAPHY

1. Ansbacher, S., Remington, R. E., and Culp, F. B. "Copper Determination in Organic Matter." *Ind. Eng. Chem., Anal. Ed.*, 3, 314-17 (1931).
2. Association of Official Agricultural Chemists "Methods of Analysis." Association of Official Agricultural Chemists, Washington, D. C. second ed. Chap. XIV, Sec. 13, 212. (1925).
3. *Ibid.*, Chapter XIV, Sec. 3, 209.
4. *Ibid.*, Chapter IV, Sec. 2, 3, 5; 39-41.
5. *Ibid.*, Chapter IV, Sec. 9, 42-43.
6. *Ibid.*, Chapter XIV, Sec. 10, 211.
7. *Ibid.*, Chapter XIV, Sec. 12, 211
8. *Ibid.*, Chapter XIV, Sec. 9, 211.
9. Benoy, M. P., "The Mineral Content of the Jujube." *J. Agr. Res.* 39, 949-51 (1929).
10. Bertrand, G., and Benson, B., "The Zinc Content of Food Vegetables" *Compt. rend.* 187, 1098-1101 (1928); *C. A.* 23, 1696.
11. Bertrand, G., and Benson, B., "The Zinc Content of the Chief Vegetable Foods." *Bull. soc. hyg. aliment.* 16, 457-63 (1928) *C. A.* 23, 2505.
12. Bidwell, G. L., and Sterling, W. F., "Preliminary Notes on the Direct Determination of Moisture." *Ind. Eng. Chem.* 17, 147-9, (1925).
13. Bunge, G., "Der Kalk - und Eisengehalt unserer Nahrung." *Ztschr. Biol.* 45, 532-39 (1904).
14. Chen, C. Y. "Vitamin C in Chinese Food Materials" *Science (China)* 15, 931-6 (1931); *C. A.* 25, 5446.
15. Clague, J. A., and Fellers, C. R. "Time - Temperature - Humidity Relations in Dried Fruit Pasteurization. *J. Bact.*, 21, 30-31 (1931).

16. Cook, A. A., and Woodman, A. G. "The Detection of Vegetable Gums in Food Products" *Ind. Eng. Chem.* 10, 530-33 (1918).
17. Dodd, A. S. "The Natural Occurrence of Boron Compounds in Fruits and Vegetable Products" *Analyst*, 54, 15-20 (1929).
18. Epperson, A. W., "The Pyrophosphate Method for the Determination of Magnesium and Phosphoric Anhydride." *J. Am. Chem. Soc.*, 50, 321-7 (1928).
19. Fales, H. A., "Inorganic Quantitative Analysis" The Century Co., New York, par. 191 (1925).
20. *Ibid.*, par. 273.
21. Fattah, M. T., "Chemical Studies of Dates." *Date Grower's Imst. Rpt.*, 4, 10-12 (1927).
22. Fattah, M. T., and Cruess, W. V. "Factors Affecting the Composition of Dates." *Plant Physiol.* 2, 349-55 (1927); *C. A.* 22, 4153.
23. Fellers, C. R., and Clague, J. A., "Souring of Dates by Yeasts." *J. Bact.* 22, 63 (1932).
24. Forbes, E. B., Beegle, F. M., and Mensching, J. E. "Mineral and Organic Analyses of Foods." *Ohio Expt. Sta. Bull.* 255 (1913).
25. Grimbert, J. (Title not known) *J. de Pharm.* 20, 485 (1889) (Reference found in) Wehner, C. "Die Pflanzenstoffe" Gustav Fisher, Jena. (1911).
26. Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis" John Wiley and Sons, Inc., New York, 394 (1929).
27. Jacobs, M. B., and Jaffe, L. "Method for Identification of the Common Gums." *Ind. Eng. Chem., Anal. Ed.* 3, 210-12 (1931).
28. Leach, A. E., "Food Inspection and Analysis" John Wiley and Sons, Inc. 4th ed., 887 (1920).

29. Lindow, C. W., and Petersen, W. H. "The Manganese Content of Plant and Animal Materials." J. Biol. Chem., 75, 169-75 (1927).
30. Lindow, C. W. Elvehjem, C. A., and Petersen, W. H. "The Copper Content of Plant and Animal Foods." J. Biol. Chem. 82, 465-71 (1929).
31. Lloyd, F. E., "Development and Nutrition of the Embryo, Seed, and Carpel in the Date." Mo. Bot. Gard. Ann. Rept., 21, 103-164 (1910); Expt. Sta. Record 24, 629.
32. McLeod, G. and Booher, L., "The Antiscorbutic Vitamin Content of Some Preserved Foods." J. Home Econ. 22, 588-93 (1930).
33. Petersen, W. H., and Elvehjem, C. A., "The Iron Content of Plant and Animal Materials." J. Biol. Chem. 78, 215-23 (1928).
34. Sherman, H. C., "Food Products" The MacMillan Co., New York . 337 (1914).
35. Ibid., 348
36. Ibid., 353.
37. Sherman, H. C., and Smith, S. L., "The Vitamins." Chemical Catalog Co., Inc., New York, . 269 (1931).
38. Slade, H. B., "Invert and Cane Sugar Dates." Rept. Ariz. Agr. Expt. Sta. 17, 164, (1906).
39. Smith, A. H., "Boric Acid Occurring Naturally in Some Fruits." Ohio. J. Sci. 17, 66-8 (1916).
40. Smith, M. C. and Meeker, L. A., "The Vitamin Content of Three Varieties of Dates." Univ. of Ariz. Agr. Expt. Sta. Tech. Bull. 34. (1931).
41. Smith, S. L. "Vitamins in Food Materials." U. S. D. A. Circ. 84 (1929).
42. Stiebeling, H. K., "The Iron Content of Vegetables and Fruits." U. S. D. A. Circ. 205 (1932).

43. Stugart, R., "Determination of Iron in Milk and Other Biological Materials." Ind. Eng. Chem., Anal. Ed., 3, 390-93 (1931).
44. Weston, W., and Levine, H. "Vitamin Chart" Ind. Eng. Chem., News Ed. 10, 31 (1932).
45. Vinson, A. E., "The Function of Invertase in the Formation of Cane and Invert Sugar Dates." Botan. Gaz., 43, 392-407 (1907); C. A. 1, 2420.
46. Vinson, A. E. "Endo- and Ekto-Invertase of the Date." J. Am. Chem. Soc. 30, 1005-20 (1908).
47. Vinson, A. E., "Chemistry and Ripening of the Date." Univ. Ariz. Agr. Expt. Sta. Bull. 66, 403-35 (1911).

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