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LIST OF SYMBOLS

ASTM	Americal Standards for Testing Materials
$(Ca)_{DE}$	Dito in the dilution extract
$(Ca)_{SE}$	Concentration of the calcium ion in the saturation extract
DP	Dilution percent
EC	Electrical conductivity in dSm^{-1} (deci Siemens per meter)
K_{SP}	Solubility product
M	Molaric concentration
R	Recovery percent
$(SO_4)_{DE}$	Dito in the dilution extract
$(SO_4)_{SE}$	Concentration of the calcium ion in the saturation extract
SP	Saturation percent
Wd	Weight of soil specimen after drying of 110c°
Ws	Weight of soil specimen after drying of 45 c°
Ws'	Weight of soil specimen after soaking and drying at 45 c°
α	Signigicance level
ε	Number of crystalline water molecules
χ	Gupsum content in %

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analysis in the extract by the standard gravimetric method using $BaCl_2$ solution. A comprehensive revising for the procedure, concentrations of the reagents, and the procedure of (SO_4^{2-}) analysis may modify the performance of the method. This is left for future work due to the limitation of time available to finish this study.

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1- Exchange error which is not taken into account in this method.
2- Ignoring that part of gypsum which dissolves in the saturation extract. This comes from the fact that the method determines the soil gypsum from the difference in concentrations of (Ca^{2+} + Mg^{2+}) in the dilution extract and the saturation extract, so it aims at that part of gypsum which not dissolved in the saturation extract.

The exchange error alone accounted about -22% as reported by Lagerwerff et al.(1965).So it is concentration of (Ca^{2+}+Mg^{2+}) was used. These findings agree well with the results of this study and the discussion above. Also the value of the mean recovery percent found here is in a good agreement with a value of (92.5) reported by Abbas (1995) in one of the two laboratories which made the analyses for his study by this method.

The method of Bower and Huss (1948) came in the fourth order as the results of this study revealed. With a mean value for the recovery percent of 72.22, this method underestimates soil gypsum by about 28%. Many researchers have reported similar assessment for this method. Al-Zubaidi and Al-Barzanji found that this method underestimates gypsum content by 0.57-9.47%. An average value of the mean recovery percent of 76.7 and 75.4 was reported by Lagerwerff et al. (1965) and Abbas (1995) respectively.

Underestimating gypsum by this method may be explained in the following paragraph.

The method specified a dilution ratio of 1:5 (water:soil). This ratio is not sufficient to dissolve all the gypsum in the specimen when the gypsum content exceeds 1.3115%, on the basis that the water solution of gypsum contains

30.5mmol$_c$ l^{-1} at 25°C at equilibrium. Most of the soils in the arid zones contain gypsum which exceeds this value. The method didn't suggest a direct way to assign the proper dilution ratio for highly gypsiferous soils. Besides that the method recommends a shaking period of 30 minutes in mechanical shaker. This period is not sufficient to dissolve gypsum completely especially when the soil is rich in gypsum and the gypsum accumulations with in the soil matrix are coarse.

Al-Zubaidi and Al-Barzanji (1981) in their study proposed a simple procedure to determine the proper dilution ratio to be used in this method depending on the electrical conductivity of the extract. They also reported that a dilution ratio of 1:300 and shaking period of 7 hours are necessary to insure complete dissolution of soil gypsum in water in many cases.

The problem of incomplete gypsum extraction from soils by water is present in all methodologies using water to extract it. This problem is associated mainly with the low solubility of gypsum where its solubility product $K_{SP}=2.44*10^{-5}$ (Nakayama, 1971). The saturated aqueous solution of pure gypsum at 25°c contains 30.5 mmol$_c$.l^{-1} as mentioned before and the electrical conductivity of this solution is 2.2 dSm^{-1}. In the presence of Ca^{2+} or SO_4^{2-} from sources other than gypsum, the solubility of the salt is less (Common-ion effect). In the case of the presence of other ions, the solubility is greater (salt effect) due to the increase of the ionic strength I of the solution (Lagerwerff et al., 1965; Al-Zubaidi, 1989; Rance and Davey, 1968).

The net result of these counteracting effect depends on the composition of the soil tested and hence on the species and concentrations of the ions available in its extract. Whenever the common-ion effect is prevailing, the gypsum solubility in water reduces and hence the gypsum content in the soil will be underestimated.

In addition to the above, the exchange error, which is not taken into account in this method will cause the gypsum finding to be less than its actual values. Also the acetone occluded in the loosely structured precipitate will suppress the EC measurement leading to underestimation of gypsum content.

Finally, the proposed method overestimates the soil gypsum by about 40%. The method in principle is similar to the method of Berigari and Al-Any. It is based on the extraction of gypsum from a 2.0 gm soil sample by 0.5M $(NH_4)_3$ PO_4 solution with the aid of ultrasonic agitation.

The increase in gypsum content as determined by this method, may be attributed to the non gypsic sulfates available in the soil. Also there is a possibility of precipitating Ba_3 $(PO_4)_2$ during the (SO_4^{2-})

time. On the contrary to the methods which use water to extract gypsum, and need high water soil ratios and long time for shaking the system with no sure of extracting the mineral entirely due to its low solubility and low rate of its dissolution in water.

The second method in the order is the method of Lagerwerff et al. (1965). With a mean value of 102.86 for the recovery percent, this method seems to be very close to the first method in the order of accuracy. And since the testing procedure here is easier than that of the above method, the author recommends it. Further more, this method utilizes, in its procedure, apparatuses which are available in most local laboratories, whereas the method of Berigari and Al-Ani needs a sonicator (Ultra-sonic agitator) in the extraction procedure. Such an apparatus is not available in most of our soil laboratories.

This method can be considered as a modification for the method of Bower & Huss (1948). Both methods extract gypsum by distilled water, but the method of Largerwerff et al. is more accurate than the method of Bower & Huss because it avoids or minimizes the following errors:-

1-Exchange error:- Diluting any soil water system causes a shift in ion-exchange equilibrium, that enriches the exchange complex with divalent cations (such as Ca^{2+}) on the expense of monovalent ones (such as Na^{1+}, K^{1+}, NH_4^{1+}), this is called valence-dilution effect. This phenomenon will cause a loss of some of the calcium ions resulting from dissolution of gypsum in water, and an underestimation in gypsum content if this error is not avoided or corrected for. The method avoids this error by using $Ca(NO_3)_2$ solution with acetone in the first step of gypsum precipitation to insure an excess of Ca^{2+} over SO_4^{2-} and so complete precipitation of SO_4^{2-} as gypsum. Finally gypsum content is determined on the basis of sulfate associated with calcium. The exchange error averaged about –22% of the uncorrected gypsum content (Lagerweff et al., 1965).

2- Error resulted form co-precipitating of lime with gypsum:-
Although the solubility of $CaCO_3$ in water is very low but still it would dissolve during preparing the soil extracts, if it is available in the soil to be tested. In this method glacial acetic acid is added to avoid the precipitation of some $CaCO_3$ in the acetone conditioned medium. Also it prevents the formation of two liquid phases whenever NaCl is present in high concentrations.

3-Occlusion error: The bulk volume of the precipitated gypsum depends on the mode of adding the reagents used in this method to the soil extracts. Accordingly this will determines the amount of occluded reagent and other salts in the precipitate. This will lead to an error when the precipitate is re dissolved and analysed to find gypsum content. This error is called occlusion errors. The densest the precipitate, the less that error is.
The occlusion ratio is defined as the ratio of the volume of occluded acetone (ml) to the weight of gypsum precipitated (gm). This ratio ranges from 5-25 depending on the mode of adding the reagent to the soil extract. The mode of slow layering the reagent on the soil extract gave the lowest value for the ratio. The occlusion error averaged about -3%.

4- Error from non gypsic sulfates:- Soil may contain non gypsic sulfate ion causing over estimation of the gypsum content if not taken into account. In this method the procedure of calculating gypsum content as given in 2-1-1-3 avoids the effect of the presence of non gypsic sulfates.

In view of the final calculation, sulfates other than that associated with Ca^{2+} as gypsum is eliminated from the results.

Following the method of Lagerwerff et al., in the order of precision is the method given in the handbook 60 of the U.S. Department of Agriculture. The mean recovery percent of the method as obtained in this study was 90.46 and hence the method underestimates gypsum content in soil by about 9.5%. Lagerwerff et al. (1965) reported similar result. This underestimation may be related to one of the followings:-

The results given in **Table (4)** show that those methods differ from each other in their ability to determine and detect the gypsum content in the soil.

The calculated content of gypsum by each of the tested method was also expressed as recovery percent (R), and given in **Table (5)**. The recovery percent is defined as:

$$\textbf{Recovery percent (R)} = \frac{\textbf{calculated gypsum content}}{\textbf{available gypsum content}} \times 100\% \qquad (5\text{-}1)$$

Table (5) Values of the recovery percent

Gypsum added %		**1**	**5**	**10**	**30**	**60**	**Mean**	**Standard deviation (SD)**
Recovery %	**Bower & Huss**	73	74.6	75.9	66.2	71.4	72.22	3.77
	Lagerwerff et al.	94	101.6	93.7	117.5	107.5	102.86	10
	U.S.D.A	81	94.2	89.5	90.4	97.2	90.46	6.12
	Berigari & Al-Ani	112	105	95.3	95.3	98.8	101.28	7.18
	Proposed	163	154.6	134.8	128.1	118	139.7	18.7

The mean recovery percent and the standard deviation which reflect the accuracy and precision were reported also for each method.

The values of the mean recovery percent indicate that the method of Berigari & Al-Ani with a mean value of (101.28) is the most accurate one of the five methods included in this study. The method has a reasonable precision represented by a standard deviation value of (7.18). Following that method in the order of accuracy is the method of Lagerwerff et al. . The mean value of the recovery percent by this method was (102.86) which is very close to the previous method. The scattering of the results in this method is more than the previous method represented by a standard deviation of (10).

The other methods can be arranged in a descending order from the accuracy point of view as U.S.D.A method, Bower & Huss method and at last the proposed method.

The U.S.D.A method underestimates the actual gypsum content by about (9.5%), whereas Bower & Huss method underestimates the soil gypsum content by about (28%). Lagerwerff et al. (1965), Al-Zubaidi & Al-Barzanji (1981) and Abbas (1995) have reported similar findings.

Discussion

In view of the statistical analyses, and within experimental variability, the precision of the method of Berigari and Al-Any is better than that of any of the other methods. The high precision of this method is attributed to the following points:-

1- Washing the soil specimen with 50% ethanol to remove the soluble non-gypsic sulfates and thus minimizing the positive error (i.e., overestimation) of gypsum. Also, this process greatly reduces the solubility of gypsum during this step of the testing procedure, and thus minimizing the negative error (i.e., underestimation) resulting from its loss with the solvent.

2- The new approach adopted in extracting gypsum from the soil specimen using Na_2CO_3 solution to convert the gypsum to the more soluble Na_2SO_4. This new technique insures the complete extraction of gypsum by not more than two equilibrations with 25ml of Na_2CO_3 solution, each

The native gypsum content of the soil used in this study was found to be very low and can be neglected. Three methods for gypsum determination were used for this purpose and the results are given in **Table (3)**. Each value represents the average of duplicate determinations.

Table (3) The native gypsum content of the soil

Method	Gypsum content %
Bower and Huss	0.01
U.S.D.A	0.03
Lagerwerff et al.	0.02

Its seems that the native gypsum content of the soil is negligible and the soil can be considered as gypsum free.

A suitable quantity of the soil was ground and passed through No.10 ASTM sieve to remove any impurities. It was then divided to five parts and each part was mixed with a quantity of pure gypsum of analar grade to give five levels of gypsum content (1%, 5%, 10%, 30% and 60%). After that each part was further ground and passed completely through No.40 ASTM sieve to ensure complete mixing and homogenizing of the soil with the gypsum added.

The gypsum content in those soils was then calculated by the five selected methods of gypsum determination.

Methods

The following four methods were selected to be evaluated in this study.

1- Bower and Huss (1948) method.
2- Lagerwerff et al. (1965) 2nd method.
3- U.S.D.A. (1954) method.
4- Berigari and Al-Any (1994) method.

In addition to the above, a fifth method was included too. This method was an attempt which was done by the author to make a modification for the method of Berigari and Al-Any. In this proposed method, all the steps are similar to those in the method of Berigari and Al-Any except that the author used ammonium phosphate solution instead of sodium carbonate solution to convert soil gypsum to the more soluble ammonium sulfate. The method will be referred to in this study as "Proposed Method".

RESULTS AND DISCUSSION

Results

The results of gypsum determination by each of the five methods for each of the five levels of gypsum content are given in **Table (4)** below. Each result represents the average of two replicates.

Table (4) Gypsum content determined by the tested methods

Gypsum added, %		1	5	10	30	60
Method of Gypsum determination	**Bower & Huss**	0.73	3.73	7.59	19.86	42.84
	Lagerwerff et al.	0.94	5.08	9.37	35.25	64.5
	U.S.D.A	0.81	4.71	8.95	27.12	58.32
	Berigari & Al-Ani	1.12	5.25	9.53	28.6	59.3
	The Proposed method	1.63	7.73	13.48	38.43	70.8

Table (1) Some chemical properties of the soil

EC dSm^{-1}	pH	Soluble ions mmol$_c$. l^{-1}							CaCO$_3$ %	Organic matter %
		Ca^{2+}	Mg^{2+}	Na^{1+}	K^{1+}	SO_4^{2-}	Cl^-	SO_3^{1-}		
2.54	7.66	6.4	2.4	3.2	0.35	1.3	8.3	nill	25.6	1.5

Table (2) Some physical properties of the soil

Specific gravity	Dry density Mg/m^3	Saturation percent SP	Saturation hydraulic conductivity cm/min	Void ratio	Liquid limit	Plastic limit	Clay sized Particles % by weight
2.65	1.43	48.86	0.023	0.85	33.8	25.5	23

The particle size distribution curve of the soil is shown in **Fig .(1)** .

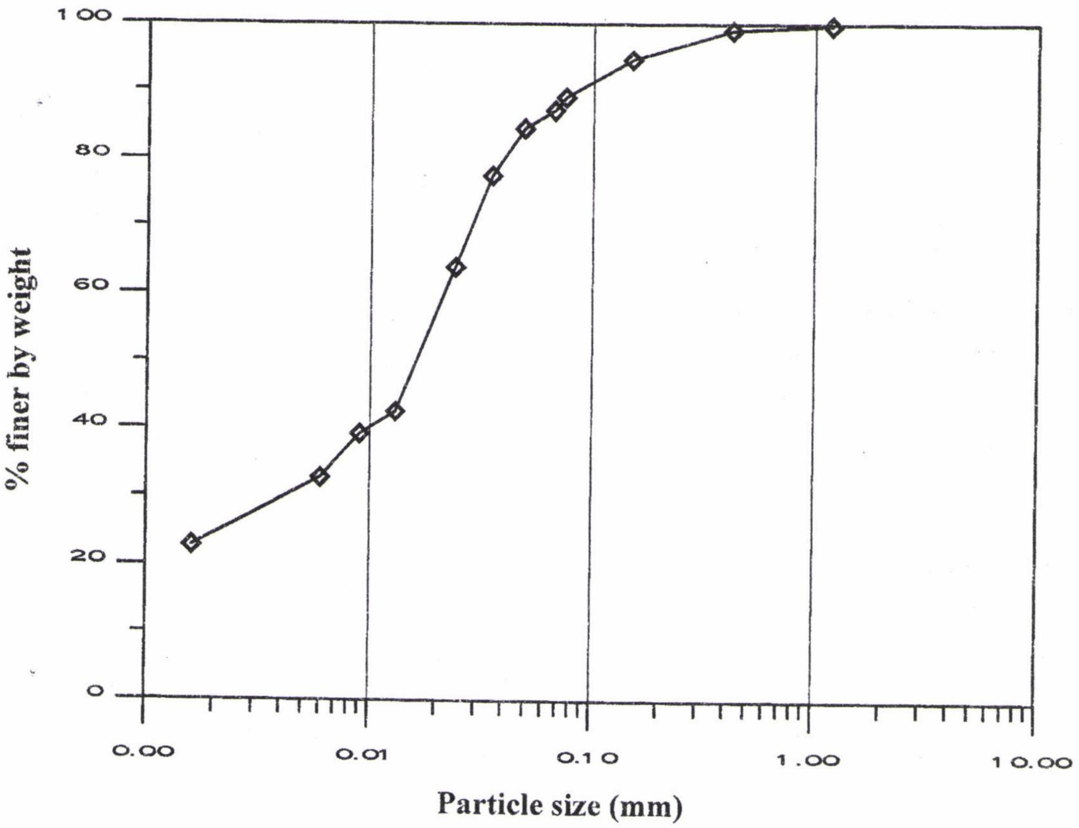

Fig. (1) Particle size distribution curve

According to the Unified Soil Classification System the soil is classified as (ML), inorganic silts and very fine sands with slight plasticity.

1- U.S.D.A. method.
2- Y.E. V.Arinushkina method.
3- Optical method.
4- Bower and Huss method.
5- T.A. Kovalinko method.

The tests were carried out in three official laboratories, and the main findings of this study were:

1- The best results of the recovery gypsum content were obtained by method (1). The author attributed that to the large soil specimen used in this method compared to the other methods.
2- Method (3) gave good average value of the percentage of the recovery gypsum but the scattering of the results (represented by the standard deviation) was large.
3-Method (2) gave higher values for the gypsum content which may be related to the use of HCl which dissolves all sulfates from sources other than gypsum.
4-Methods (4) and (5) gave gypsum contents which are much lower than the real values.

Berigari and Al-Any (1994) in their proposed method for gypsum determination proposed a procedure for gypsum extraction by converting it to more soluble sodium sulfate as explained in item 3-1-3-3. Gypsum content was determined from SO_4^{2-} analysis by two methods: -

a- The standard gravimetric $BaSO_4^{2-}$ method.
b- The turbidimetric method.

To evaluate their proposed method, they extracted gypsum with water, then determined SO_4^{2-} by two methods.

c- The turbidimetric method.
d- The Bower-Huss conductometric method.

In brief, they examined two methods of extraction and three methods of SO_4^{2-} analysis.

They concluded that the method of extraction was the major reason for the deviation of methods c and d from methods a and b. Also they found that methods c and d displayed lower precision given by the coefficient of variation (CV) ranges (3.1– 8.2 and 3.7–11.0%) respectively compared to the values of (CV) for methods a and b which were (1.3 – 5.1 and 1.1 – 3.8 %) respectively.

Finally they recommended their new method of gypsum extraction and its determination from turbidimetric SO_4^{2-} analysis because it is simple, rapid, accurate and very efficient (Berigari and Al-Any, 1994).

COMPARASION OF SOME SELECTED METHODS

An attempt was made to evaluate some methods which were selected from the ones presented in this study. An artificial gypsiferous soil was used for this purpose. A description for the materials and methods is given below

Materials

In order to compare the methods mentioned in the previous section, a gypsum free soil was gypsofied by adding pure gypsum ($CaSO_4.2H_2O$) of analar grade in specified percentages.

The soil was obtained on July 2002 from a field in the campus of Baghdad University. The depth of the sample was 0-30 cm, the sample was well above the ground water at that time of the year. Investigating the soil at the site shows that the soil there belongs to TW455 soil series (silt loam) according to Al-Agaidi (1976) classification. Some of the chemical and physical properties of the soil are given in **Tables (1&2)** respectively.

for the semi-quantitative determination of the gypsum in soil. Schultz (1964) proposed a method for semi-quantitative estimates of bulk mineralogy. Skarie et al. (1987) reported that this technique is inaccurate for a quantitative determination because of the preferred orientation of gypsum crystals which require replications of sample and tedious counting procedure.

Quantitative Determination (Friedel, 1978)

The (020) X-ray reflection of gypsum at 7.56 A^{0} is nearly specific and may be used for detection and quantitative measurement of the mineral in soil samples. Here measurements references may be prepared from sample parts by dehydration of the original gypsum and adding known quantities of this mineral. This is important in the quantitative measurement by powder diffractometry of a mineral with low hardness and good cleavage. Under comparable condition for sample and reference, gypsum content can be determined in the range of 0.5-20%. (FAO Bull. 62. 1990).

PREVIOUS STUDIES TO EVALUATE SOME OF THE MENTIONED METHODS

Al-Zubaidi and Al-Barzanji (1981) evaluated the following four methods which are widely adopted to the routine testing in the local laboratories:-

1- Bower and Huss method.
2- Lagerwerff et al. (1st. Method).
3- Lagerwerff et al. (2nd. Method).
4- YE. V. Arinushkina method.

They used artificial gypsiferous soils (gypsum free soils mixed with specified quantities of gypsum), then they tested these soils by the selected methods and the calculated gypsum content was compared with the real values.

The main findings of this study were:-

1- The best method which gave the closest estimation of the gypsum content to the real values was the 1st method of Lagerwerff et al.. The method was suitable for testing soils with any gypsum content. The error in this method was less than 5%. Using acetic acid with acetone in this method reduced the error resulting from the possibility of precipitating lime with gypsum when acetone is used alone, since lime does not precipitate in acidic medium. The addition of calcium nitrate to the extract reduced the valence-dilution effect for samples with high gypsum content. Such samples need wide soil : water ratio (more than 1:300) to insure precipitation of sulfate as gypsum, even at high dilutions.

2- The method of YE. V. Arinushkina, in which gypsum is extracted by hydrochloric acid, overestimated gypsum by about 5% .

3- To dissolve all gypsum in water, the soil-water mixture should be shaked for 7 hrs at least.

Abid-Alkarim (1993) examined the following four methods of gypsum determination: -

1- Bower and Huss method.
2- U. S. D. A method.
3- Acid resins method.
4- Lagerwerff et al. (1965) (1St. method).

He used natural gypsiferous soils having a gypsum content varying within the range (1 - 60)%. It is found that Lagerwerff et al. method was the best method. Bower and Huss method underestimates the gypsum content with an error ranging between (0.4 – 14.2)%.

U.S.D.A. method and Acid resins method overestimated the gypsum content with a maximum error of 15.9 % and 3.8 % respectively.

Sirwan (1989), in a study to compare the method of YE. V. Arinushkina with that of Bower and Huss, found that the first method estimated gypsum higher than the second method by (5% - 26%).

Abbas, H.O. (1995) used artificial gypsiferous soils with gypsum content of [3%, 5%, 10%] to evaluate the following methods:

increments of distilled water. The solution and the washings shall be collected and titrated against sodium hydroxide solution, and the percentage of sulfate as (SO_3) is calculated accordingly. Gypsum content then can be calculated on the basis of the SO_3 content. The method cannot be used if the soil or the ground water contains chloride, nitrate or phosphate ions.

Stern et al. (1989) used Na^+ and Cl^- resins to dissolve all the gypsum in the soil sample and release soluble Ca^{2+} and SO_4^{2-} ions. Any one of these ions can be measured and the gypsum content in the sample then can be determined.

Determination of SO_4^{2-} by Ion Chromatography

The current trend in most laboratories is to analyze SO_4^{2-} by ion chromatography (Dick and Tabatabai, 1979; Marko–Varga et al., 1984; Nieto and Frankenberger, 1985). Chromatographic analysis separates various anions in an exchange column according to their selectivity for a given exchange resin. This method not only provides an improved sensitivity over previous methods, but also allows for the simultaneous determination of several inorganic anions (Skarie et al., 1987).

The gypsum content calculated in two ways, based either on Ca^{2+} or SO_4^{2-}, measured by single column ion chromatography in a sufficiently dilute extract to dissolve completely the gypsum present in the soil sample shows some different results (Skarie et al., 1987). For highly chloride soils, gypsum contents based on Ca^{2+} determination are essentially equal to results based on SO_4^{2-} data, but for sulfate soils, gypsum contents calculated from Ca^{2+} measurements are generally lower than those from SO_4^{2-}, due to adsorption of Ca^{2+} on the exchange complex (exchange error) during the extraction process.

Thermogravimetric Methods

Thermogravimetric analysis or what so called Differential Thermal Analysis (DTA) is based on the loss of weight when a sample containing gypsum is heated. The loss of weight is due to the dehydration of gypsum. A large amount of hydration water molecules are lost if gypsum is heated to 170 C°, forming Plaster of Paris (Basanite) $CaSO_4.\frac{1}{2}H_2O$, but if heating continues to more than 200 C° , anhydrite starts to form with the hydration water being last completely (Al-Mufty 1997). These methods are recommended when the gypsum content is high (Eswaran & Zi-Tong 1991) and they yield better results than the standard acetone method. They can be considered as good semi-quantitative methods, which commonly overestimate gypsum content. These methods are recommended when the sample contents more than 8% of gypsum (Porta, 1998).

Nelson et al. (1978) proposed a method for gypsum content determination based on this principle. In this method gypsum content is determined from the loss of crystal water upon heating to 105 C°. The method is sufficiently accurate for taxonomic uses (FAO Bull. 62, 1990).

Al-Mufty and Nashat (2000) have proposed a similar method. In this method the degree of hydration of soil gypsum is taken into account through calculating the number of crystallization water molecules in gypsum molecule.

Gypsum Determination by X-Ray Diffraction Techniques.

Gypsum can be identified by X – ray diffraction techniques (Khan & Webster 1968) on oriented samples (sedimentation technique). The X-ray diffractometry can be used for semi-quantitative identification and quantitative determination of gypsum content. However, these methods are not adopted in routine works because they need complicated instruments and highly qualified staff which are not easily available in all laboratories. Furthermore, the results of these methods are not recommended because of their proximity.

Semi-Quantitative Gypsum Identification

Gypsum in soil can be identified by X - ray diffraction with potassium chloride as an internal standard. Ratios of counts on diffraction peaks of maximum intensity for gypsum and KCl are used

1- More accurate than other methods .
2- Many samples can be tested in short time
3- Non gypsic sulfate will interfere the results.
(Abbas 1995).

Berigari and AL-Any (1994) Method

This method is based on modern thermodynamic principles.

a- Wash 2.0 gm of soil once with 25ml portions of 50% (V/V) ethanol to selectively remove nongypsic soluble sulfates while reducing the solubility of gypsum. Centrifuge and decant the supernatant.

b- Suspend the sediment in 25ml of 0.5M Na_2CO_3 solution by 30 second of sonification, to disturb the formation of stable $CaCO_3$ coating on gypsum particles.

In this state, the soil gypsum which is a sparingly soluble salt will be converted to water soluble sodium sulfate (Na_2SO_4) according to the reaction

$$CaSO_4.2H_2O_{(s)} + Na_2CO_{3\,(aq)} \qquad CaCO_{3\,(s)} \rightleftharpoons + Na_2SO_{4\,(aq)} \downarrow + 2H_2O \quad (2\text{-}4)$$

The solubility of $CaCO_3$ in water is much lower ($K_{SP} = 5.03 \times 10^{-9}$, Nakayama 1971) than that of gypsum ($K_{SP} = 2.44 \times 10^{-5}$, Nakayama 1971) . The addition of water soluble carbonate salt solution such as Na_2CO_3 solution in excess to a system containing gypsum , the common ion effect (CO_3^{2-}) will cause continuous precipitation of Ca^{2+} as $CaCO_3$. This will reduce the concentration of Ca^{2+} ion in the system leading to continuous dissolution of gypsum. The net effect is total conversion of gypsum Ca^{2+} to $CaCO_{3\,(s)}$ leaving behind the SO_4^{2-} in solution.

c- Centrifuge the supernatant solution at 1000 × g and 25°c, then filter.

d- Determine sulfate content in the aqueous extract by standard $BaSO_4$ gravimetric or turbidimetric methods.

e- Gypsum content in the soil is calculated from SO_4^{2-} analysis assuming that all the SO_4^{2-} in extract came from soil gypsum.

Determination of SO_4^{2-} from Dissolution of Gypsum in Acid

A hot dissolution of gypsum in hydrochloric acid, precipitation of sulfate ion with Ba^{2+} , and gravimetric determination of barium sulfate are the basic lines of this method. The use of acid here assures the solubilization of all the gypsum in the sample even if it is coated by $CaCO_3$ (Keren and Kanschansky, 1981).

The method proposed by Arinushkina (1962) is an example of these methods.

Acid Resins Methods

In these methods, soil sample is mixed with concentrated acid resins saturated with hydrogen, which will exchange with cations of soil salts leading to the formation of sulferic, hydrochloric and carbonic acids. The total acidity is measured from calibration with sodium hydroxide, and this will include sulferic and hydrochloric acids only since carbonic acid will soon dissociate into water and carbon dioxide , and hence will not affect the measurements. After measuring the chloride concentration , the sulfate concentration can be determined from the difference between the total acidity and chloride concentrations. Then gypsum content in the soil can be determined from the sulfate content (Abbas 1995).

Test No. 10 of British standard No.(1377:1975)is devoted for the measurement of the sulfate content of ground water and of aqueous soil extracts using strongly acidic cationic exchange resins such as Zeo-Karb 225 or Amberlite IR-120. A 100 ml of the ground water or 25 ml of the soil extract shall be boiled for 5 min., left to cool. The solution shall then be passed through an ion-exchange column filled with the activated acid resin, and the column rinsed with two 75 ml

A correlation exists between $CaSO_4$ concentration and the electrical conductivity of the solution. For a saturated aqueous solution of pure gypsum at 25°C, the electrical conductivity is 2.2 dSm^{-1}, equivalent to 30.5 $mmol_c\ l^{-1}$. In presence of Ca^{2+} or SO_4^{2-} ions coming from sources other than gypsum, the solubility of gypsum is less due to the common-ion effect, whereas, in the presence of other ions, the solubility is greater due to the salt effect (Lagerwerff et al., 1965; Gobran and Miyamoto, 1985; Al-Zubaidi, 1992 ; Porta, 1998).

Lagerwerff et al. (1965) modified the Bower and Huss (1948) method to avoid the exchange error by determining gypsum on the basis of sulfate associated with calcium; this minimizes errors due to acetone and to occluded ions. In salt affected soils, salts can interfere with electroconductometric measurements (Hesse 1971).

The methods falling under this category are:-

Bower and Huss (1948) Method

a- Dissolve soil gypsum in distilled water using a soil : water mixture enough to dissolve all gypsum in the specimen .
b- Precipitate gypsum in the extract obtained from the previous step by adding acetone.
c- Dissolve the precipitate using distilled water.
d- Measure the electrical conductivity (EC) of the solution and determine the gypsum content from a standard curve relating gypsum concentration in the solution to the electrical conductivity.

The disadvantages in this method as given by Al-Zubaidi and Al-Barzanji (1981) are :-

1- The mixing ratio soil : water of 1: 5 suggested by the authors is not sufficient to dissolve all gypsum present in most soils . Higher ratios (up to 1: 300) may be needed in highly gypsiferous soils .
2- The occlusion effect.

This method gives an approximate determination of gypsum content (FAO Bull. 62, 1990) .

Sayegh et al. (1978) Method

Lagerwerff et al. (1965) 1st Method

Determination of SO_4^{2-} from Diluted Soil:Water Extract

Here, gypsum content is determined from the concentration of SO_4^{2-} ions in the soil extract obtained after treatment of the soil specimen with a quantity of water enough to dissolve all the gypsum. Many methods are available in the literature adopting this principle in gypsum determination. These methods differ from each other by the way of detecting the SO_4^{2-} content of the soil extract. Turbidimetric (optical) and gravimetric methods are often used. A brief presentation for the methods falling under this category is given below.

The $BaSO_4$ Method (Richards 1954)

The Amended ($BaSO_4$) Method (Coutinet 1965, cited in FAO Bull. 62, 1990)

Turbidimetric (optical) Method (Head 1982)

After extraction of the soil sample , sulfate content in the extract is determined from its turbidity by the measurement of its transparency for light by means of an apparatus called " turbidity meter ".

The apparatus is calibrated first using three standard sulfate solutions of known concentrations . From the measurement of the turbidity of these solutions , a calibration curve is obtained relating concentration to turbidity. Measuring the turbidity of any extract of unknown sulfate content , its content of sulfate can be obtained from the mentioned calibration curve. Gypsum content in the extracted soil sample is then calculated by the principles of analytical chemistry. This method is characterized by :

Lagerwerff et al. (1965) 2nd Method

Lagerwerff et al. (1965) proposed this method to determine gypsum content.

a- Prepare a saturated soil paste and calculate the percent of water content in the paste (SP) on the bases of air-dry soil weight, prepare a diluted soil-water mixture using an amount of distilled water sufficient to dissolve all gypsum in the soil sample used. Calculate the ratio of water soil in percent (Dp) in this mixture. Extract the saturated soil paste and the diluted soil-water mixture.

b- Determine Ca^{+2}concentration in the saturation extract ($Ca)_{SE}$ in $mmol_cl^{-1}$ by titration with EDTA (Richards 1954-Method 7).

c- Determine sulfate concentrations in the saturation extract ($SO_4)_{SE}$ and in the diluted extract ($SO_4)_{DE}$ as given below :

1- Pipet 5 ml of each of the extracts into separate centrifuge tubes.

2- Add about 10 ml of solution A(80% acetone and 20% glacial acetic acid , and 0.05 N with respect to $Ca(NO_3)_2.4H_2O$) . Stopper the tube and shake thoroughly by hand . Centrifuge for 5 min. ,decant and invert the tube on filter paper to drain for 5 min..

3- Add 10 ml of solution B (80%) acetone and 20% deionized water), shake until precipitate is well dispersed. Centrifuge decant and drain as before.

4- Add an amount of water sufficient to dissolve the entire precipitate transfer the solution into a beaker and titrate for Ca with EDTA.

d- Small part of the soil gypsum will dissolve in the saturation extract. This part is calculated from the smaller value of the concentrations of sulfate and calcium in that extract, i.e. the smaller one of either $(SO_4)_{SE}$ or $(Ca)_{SE}$.

e- The major part of gypsum will dissolve in the diluted extract and can be calculated from the difference between sulfate concentrations in the diluted and saturation extracts, i.e. $[(SO_4)_{DE} - (SO_4)_{SE}]$.

f- The total gypsum content is determined by adding the two parts. The following equations can be used to determine the total gypsum content (χ) in the soil as a percent.

$$\chi = (SO_4)_{DE} \times DP/1000 \times 0.086 \qquad (2\text{-}1)$$

when $(SO_4)_{SE} <= (Ca)_{SE}$

$$\chi = \{(SO_4)_{DE} \times DP/1000 - (SO_4)_{SE} \times SP/1000 + (Ca)_{SE} \times SP/1000\} \times 0.086 \qquad (2\text{-}2)$$

when $(SO_4)_{SE} > (Ca)_{SE}$, because of the presence of (SO_4^{2-}) from other sources .

In this method, acetic acid is added with acetone to prevent the composition of two phases of the liquid, especially when the tested soil contains NaCl. It also prevents precipitation of $CaCO_3$ with gypsum by acetone. Calcium nitrate is added to insure that the calcium will be more than the sulfate, hence all sulfates shall be precipitated as gypsum.

Kovalenko (1972) Method

Deb (1963) Method (cited in Hesse 1971)

Electroconductometric Determination of Gypsum

The amount of gypsum present in soil can be determined by a rapid conductance method (Bower and Huss, 1948 ; Richards, 1954). Here a diluted soil:water mixture is prepared using a water : soil ratio high enough to dissolve all the gypsum available in the soil specimen. The gypsum dissolved in an aliquot of the extract is precipitated by adding acetone, and then the precipitate is redissolved in distilled water completely and the electric conductivity of the solution is measured.

water-saturated soil paste (Lagerwerff et al. 1965). For these reasons, the soil sample must be ground, and the ratio water:soil must be high, and the contact time between soil and water long enough to dissolve all the gypsum (Van Reeuwijk 1987).

If the electrical conductivity of the solution EC is less than 2.2 dSm^{-1}, then all the gypsum present in the sample should be dissolved without problems in the extraction (gypsum content less than 0.2%); if EC is 2.2 dSm^{-1} and both Ca^{2+} and SO_4^{2-} are present in concentrations about 30-32 $mmol_c\ l^{-1}$, then the saturation extract is likely to be saturated with gypsum and a more dilute extract is required to dissolve it completely (Porta 1998). If EC is more than 2.2 dSm^{-1} and Ca^{2+} and SO_4^{2-} are present in concentrations more than 30-32 $mmol_c\ l^{-1}$, then other salts more soluble than gypsum are present.

Other methods utilize the use of resins to calculate soil gypsum. Test No. (10) in the (B.S.1377:1975) used strongly acidic cationic exchange resins (such as Zeo-Karb 225 or Amberlite IR-120) in an ion –exchange column to determine sulfate content in aqueous soil extracts from which the soil gypsum content can be determined. Stern et al. (1989) used Na^+ and Cl^- resins to dissolve all the gypsum in the specimen and convert it to soluble Ca^{2+} and SO_4^{2-} ions. Any one of these ions can be analyzed by suitable method to calculate the gypsum content in the specimen.

So it can be said that gypsum determination by the wet chemical methods is generally a two steps process:

a- Extraction step in which soil gypsum is dissolved in water or acid or by converting it to more soluble salt using certain chemical treatments based on thermodynamic principles. As a result, gypsum will be transferred to an aqueous solution.

b- Analysis step in which the concentration of one of the ions resulting from gypsum dissociation (i.e. Ca^{2+} or SO_4^{2-}) in the aqueous extract is determined from which the gypsum content is found using the principles of analytical chemistry.

According to the above presentation, the wet chemical methods are further classified into the following subgroups.

Determination of Ca^{2+} from Dissolution of Gypsum in Water

The dissolved gypsum by shaking the sample with water may be selectively precipitated from the extract by adding acetone. The precipitate is redissolved in water and the gypsum is determined by measuring the Ca^{2+} concentration in the solution. Calcium ions from other soluble salts will interfere with the results (common-ion effect and salt effect), and the content of gypsum would be overestimated in these cases. Other factor, the loss of Ca^{2+} to the exchange complex (exchange error), would lead to the under-estimation of gypsum content (Lagerwerff et al., 1965; Skarie et al., 1987). The methods based on this principle are summerized below.

U.S.D.A. (1954) Method

Richards (1954) described this method in the U.S. Department of Agriculture Handbook No.60 (1954). It is called locally the dilution method. The main steps of this procedure are :-

a-Prepare a saturated soil paste and find the concentration of $(Ca^{2+}+Mg^{2+})$ ions in the extract by titration. This is called the soluble $(Ca^{2+}+Mg^{2+})$.

b- Prepare another water extract using a moisture content sufficient to dissolve all the gypsum present in the soil. This mixture is called the diluted soil: water mixture. Determine the concentration of $(Ca^{2+}+Mg^{2+})$ in the diluted extract.

c- The gypsum content is determined from the difference between the two concentrations .

The disadvantages in this method are:-

1- There is no direct method to specify the proper dilution ratio (water : soil ratio).

2- ii. The valence - dilution effect.

related to the continuous and slow dissolution of gypsum by seeping water through the gypsum-containing soil.

The presence of gypsum in soil affects its engineering properties, and behavior in a degree which is greatly dependant on the amount of gypsum present in the soil.

So the first question which arises, when dealing with such soils, is "How much is the gypsum content of the soil?"

The volume of the problem and the nature of solutions and amendments that must be done is directly related to the answer of this question. Besides gypsum in soils is important from several standpoints. Its content is used as a basis for classifying soils at the family levels. The content of soil gypsum has been related to geomorphic surfaces, tectonic phenomena and the soil age (Sayegh et al., 1978).

Due to its importance, several methods have been developed to determine gypsum content in soils. It can be said that gypsum is the most soil mineral for which determination methods have been developed (Al-Zubaidi and Al Barzanji, 1981). The precise determination of gypsum in soils is rather difficult because of the inherent errors involved in the methodologies used for this purpose (Richards, 1954).

In the followings, a presentation for the methods which are used to identify and determine gypsum content in the soil found in the available literature.

DETERMINATION OF GYPSUM CONTENT

Numerous methods for gypsum content determination are available in the literature that vary in accuracy, precision, sensitivity, and speed of analysis (Berigari and Al-Any 1994). The available methods can be grouped according to their basic principals of gypsum determination into three categories. The following paragraphs demonstrate these categories and the main methods falling in each category. The main steps of the testing procedure of the four methods included in the comparative study carried on here are mentioned. Other methods are mentioned only. If the reader is interested in any of these methods, he can review its detailed procedure in the related reference mentioned in this paper.

Wet Chemical Methods

Most of the available methods fall in this category. These methods are widespread due to their relative simplicity. They can be practiced in most laboratories because they do not require complicated or specially designed apparatus. The basis of most these methods is the dissolution of gypsum in water, there after, gypsum content is determined by a suitable analysis for SO_4^{-2} or Ca^{2+} concentration by the available methods (Porta 1998).

The precise determination of gypsum in soils is made difficult if not possible because of the inherent errors involved in extraction of the mineral by water (Bower and Huss, 1948). Studies by Reitemeier (1946) and others showed that at least three factors other than solution of gypsum may influence the amounts of calcium and sulfate extracted from gypsiferous soils. These factors are :

1- The solution of calcium from sources other than gypsum.
2- Exchange reactions in which soluble calcium replaces other cations such as sodium and magnesium.
3- The solution of sulfates from sources other than gypsum (Richards, 1954; Loveday and McIntre, 1974).

Some authors proposed a selective removal of the nongypsic soluble sulfates by ethanol prior to gypsum dissolution (Berigari and Al-Any, 1994).

In the wet chemical methods, all the gypsum in the sample must be dissolved. Due to its low solubility in water, high water:soil ratio will be required. Moreover, the dissolution rate of gypsum in water increases as the finess of the crystals increases (Kemper et al. 1975). The relatively low solubility of gypsum in aqueous systems suggests that it may be present as crystalline material in

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COMPARSION OF SEVERAL METHODS FOR DETERMINATION OF GYPSUM CONTENT IN SOILS

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ABSTRACT

Due to the solubility of gypsum, gypseous soils are known to be very problematic for civil engineers.

To assign the volume of the problem and the manner of dealing with it, it is essential to estimate the amount of gypsum in the soil as accurate as possible .The aim of this study is to highlight the methodologies available in the literature that are used to detect the presence of gypsum in soil and to determine its content . The study involves a comparison among four of the most popular methods used to determine the soil gypsum . The four methods were used to recover the soil gypsum in gypsofied soil samples containing known amount of gypsum . The analyses for the test results showed that the method proposed by Berigari and Al-Any (1994) was the most accurate one .

خلاصة

تعتبر الترب الجبسية من أكثر الترب المسببة للمشاكل للمهندسين المدنيين ، ولتحديد حجم المشكلة وكيفية التعامل معها فأن من الضروري تخمين نسبة الجبس الموجودة في التربة بأكثر دقة ممكنة .

تهدف هذه الدراسة الى تسليط الضوء على الطرق المتوفرة حالياً والتي تستخدم للتحري عن وجوْد الجبس في التربة وتحديد نسبته . أضافة لذلك فقد تضمنت الدراسة مقارنة بين أربعة من الطرق شائعة الاستخدام لهذا الغرض ، هذه الطرق استخدمت لحساب نسبة الجبس في نماذج تربة مجبسة بأضافة نسب معلومة من الجبس . وقد أظهرت تحليلات النتائج المختبرية بأن الطريقة المقترحة من قبل بريكاري والعاني (1994) كانت أكثر تلك الطرق دقة .

KEY WORDS
Comparisons, determination, gypsum, Methods, Soil.

INTRODUCTION

Gypsiferous soils are problematic ones from the engineering point of view. There are many problems that have been noticied when structures were constructed on gypsiferous soils in the last three decades in Iraq . These problems are related to collapsing of the soil, increasing leakage of water throw the soil, softening of the soil and attack of sulfate on concrete. All these problems are