A simple model for rapid gypsum determination in arid soils

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Abstract The development of a reliable, fast and inexpensive method to determine the gypsum content in soils to understand their behavior is crucial. However, current methods of determination are cumbersome, lengthy and imprecise. This study was conducted to develop a rapid and simple method to determine soil gypsum content. A gypsum content of 120 soil samples was determined by three methods; (1) standard silica-gel; (2) acetone; and (3) the proposed method (OMRAN GypSim). These methods were further tested for the recovery of known amounts of pure gypsum (over the range of 0–100%). The proposed method estimates the gypsum content of water loss in the soil sample by heating at 70 °C and 135–150 °C. Sandy and clay minerals mixed with gypsum reagent powder (over the range of 0–100% gypsum) were used as a reference. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), after heating at 150 °C, dehydrates, losing the two water molecules and becoming mostly anhydrite (CaSO_4). The crystal water of gypsum is not lost when the gypsum is dried at 70 °C for 45 min., whereas it is lost when the gypsum is heated at 150 °C for 15 min. The reproducibility of the proposed method is worth highest (average 0.10) followed by silica-gel (average 0.35) and acetone (average 0.47). This simple, yet effective methods determined gypsum content to within 1%, whereas other methods exceeded gypsum content by as much as 10%. An easy-to-use graphical user interface has been designed for the model running in a user-friendly way.

Keywords Gypsum · Silica-gel · Crystal water · Hygroscopic water · Prediction, Modeling

Introduction

Gypsum is widespread in both arid and semi-arid regions. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is found over a wide range of temperatures, but most gypsic soils occur in xeric, ustic, and aridic soil moisture regimes (FAO 1990). It is the most common sulfate mineral in soils. Gypsum has several undesirable effects due to its solubility. A concentration of >10% gypsum significantly interferes with soil characteristics such as structure, consistency, and water-holding capacity, while soils with more than 25% gypsum do not provide a good medium for plant growth. As a calcium-based mineral, gypsum inhibits the uptake of zinc, magnesium, iron, copper, and phosphorus in plants, resulting in nutrient deficiencies. The cation-exchange capacity is reduced, and thus the level of fertility is lowered. Re-precipitation of gypsum can result in root and water restrictions in the soil and can cause increased salinity above a gypsum pan. The somewhat high solubility of gypsum increases the osmotic potential of the material. As a result, the availability of water to plants can be decreased. Gypsum has also a considerable influence on soil properties (Visconti et al. 2010). When it is the main component of the soil, it controls its behavior. Some gypsiferous soils have been characterized by utility limitations such as the sinkholes formation (Omran 2012; Reda 1995). High water table can dissolve gypsum in the soil. Irrigation in areas with gypsum also can result in dissolution. The material goes into solution or easily erodes and forms solution cavities, pipes, and gullies. Gypsum can go into solution and then reprecipitate. Soil gypsum occurs in various forms

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in the field, according to the mode of formation (Reda 1995): small and large crystals, veins, soft powder or spots, patches, segregations or thread-like, and gypsum layer. An accurate measurement of gypsum in soil is very important because it affects many soil properties, which in turn influence management, classification, and suitability of the soils. Therefore, it is necessary to quantify accurately the amounts of gypsum in soils.

A review of the literature reveals that the previous theoretical or experimental work, which has been undertaken to determine the gypsum content in soils is rare. In terms of theoretical modelling, current methods of gypsum determination in soils, which are cumbersome and imprecise (Lebron et al. 2009), could be grouped into; wet chemical; X-ray diffraction and loss of crystal water (Farg 1999). Wet chemical methods are laborious and subject to errors due to cation exchange and occlusion of dissolved salts in precipitation (Skarie et al. 1987; Artieda et al. 2006). Also, wet methods are unsuitable for soils rich in gypsum or containing other sulfates (Herrero et al. 2016). Mahabadi and Givi (2008) evaluate different methods of gypsum determination, which the method of sodium carbonate is the most accurate one. Acetone, calcium magnesium difference, and diluted extracted sulfate methods are not sufficiently accurate. The acetone method could be considered the most reliable but very lengthy (Elprince and Turjoman 1983). Sulfate determinations by titrimetric, photometric, and luminescence methods requiring difficult-to-access and expensive reagents for their use are extremely complex, labor-intensive, and lengthy. An X-ray diffraction technique for gypsum determination (Weindorf et al. 2014) has problems of preferred orientation of gypsum and the replicates needed for counting (Khan and Webster 1968).

Methods based on the loss of crystal water of gypsum, do not rely on SO_4 determinations and thus estimate the gypsum content without interference by other sulfate minerals contained in the soil sample. The thermogravimetric methods of gypsum rely on the measure of the crystal water content of gypsum. Typically, the value 20.91% (w/w) is used; however, because not all the water is recovered at the heating temperatures used in the laboratories. The concept of a recovery (19.42%) factor (Burns et al. 2002) is useful when describing the analytical methods based on the loss of crystal water. (Nelson et al. 1978) realized the limitations of the method in low gypsum content soils, which minimizes the usefulness of the measure for taxonomic purposes, considering that the threshold for the gypsic horizon stated by Soil Survey Staff (2010) is 5% gypsum content. Elprince and Turjoman (1983) realized that the silica-gel method seems simple but slow in the proceeding. When the sample is heated to 105 °C, part of the crystal water of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is lost, and

bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is produced. With increasing temperatures, all gypsum is transformed into anhydrite (CaSO_4).

All these methods have their limitations and advantages, but most are associated with large errors (Porta 1998). Al-Awajy et al. (1994) criticized all these methods and recommended none of them to be the best. So, traditional gypsum determination methods, which are lengthy, labor-intensive, and insufficiently accurate appear to be increasingly irrelevant to many users and does not have a market for land managers and policy makers (Omran 2008). A reliable and environmentally friendly method is needed to rapidly detect and analyze soil gypsum. A growing demand for the development of more timely and cost-effective methods for quantifying gypsum in soil with reliable precision, lead us to a research question: Can we develop a more accelerated, simple, and accurate measure replace the out-of-date techniques for soil gypsum determination and suitable for soils with gypsum content as low as 5%?

Thermal changes of gypsum

Calcium sulfate occurs in three different hydrates: dihydrate (DH: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate (HH: $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and anhydrite (AH: CaSO_4). The thermal increases the gypsum transformation into bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). When soil with 50% gypsum in its fine earth fraction was heated at 205 °C, it is partly changed into bassanite. Bassanite could not be found in the samples heated at 105 °C, but it was in those heated at 205 °C (León et al. 2014). When the gypsum is heated up to 105 °C, only a small fraction (13–19%) of gypsum is removed. Subsequent partial rehydration in the laboratory results in the formation of bassanite at relative moisture below saturation (Lebron et al. 2009; León et al. 2014). At 105 °C, the gypsum crystal loses 13–19% of its mass (Artieda et al. 2006), corresponding to the two water molecules. Lebron et al. (2009) concluded that the temperature at which total water disappears is around 163 °C, since fast heating does not allow enough time for the water to diffuse through the crystal. Therefore, in the mineralogical analysis bassanite did not appear until temperatures achieved 205 °C (León et al. 2014). The transition temperature for the change from gypsum to anhydrite when in contact with water is provisionally placed at 38 °C.; for the change from gypsum to hemihydrate, when in contact with water, is most definitely placed at 98 °C. Anhydrite has been obtained experimentally from gypsum in contact with water at 100 °C. It is confirmed that the only two solids existing in the system between 0 and 200 °C are gypsum and anhydrite.

calculated according to the equation of Nelson et al. (1978).

3. The proposed accelerated method. In this method, each soil samples was placed in a Pyrex dish and dried over 70 °C in an oven for 45 min. and then heated at 150 °C for 15 min. The differences between the two weights gave a practical way to gypsum determination in soils.

Rapid and low-cost gypsum determination method

Low-cost gypsum determination using gypsum simulation (OMRAN GypSim) model was developed and implemented. In this method, the loss in water after heating at 70 °C for 45 min. and after heating using different temperature degrees (over the range of 60–150 °C) were compared. The results indicate that heating at temperature 70 °C for 45 min. equal to silica-gel for 48 h and heating at temperature 105 °C for 24 h equal to heating at temperature 135–150 °C for 15 min. So, for a rapid and simple method, heating at temperature 70 and 150 °C is simple, more rapid, and accurate.

The procedure for the proposed method to estimate soil gypsum as follows:

- 1- 10–20 g of 2-mm air-dried soil was transferred to a Pyrex dish and weighed to the nearest 0.001 g. The dish was placed in an oven at 70 °C for 45 min.
- 2- Then the dish containing the sample was placed in an oven at 150 °C for 15 min (the time depends on the oven volume and the number of samples put in the oven, the oven must have ventilation).
- 3- After the removal from the oven and before weighing, the sample was cooled completely in a desiccator. The gypsum percentage in the sample was calculated by the following equation:

$$\begin{aligned} \text{Gypsum\%} &= (W_{70} - W_{150}/W_{70} - W_d) \\ &\quad * 100 (100/19.66) \\ &= (W_{70} - W_{150}/W_{70} - W_d) * 508.65. \end{aligned} \quad (1)$$

where W_{70} = weight of the sample dried at 70 °C plus Pyrex dish, W_{150} = weight of the sample dried at 150 °C plus Pyrex dish, W_d = weight of the Pyrex dish, and 19.66 is the recovery factor of gypsum between 70 and 150 °C.

Gypsum converts slowly to hemihydrate in air at about 70 °C, and more rapidly above 90 °C and at higher temperature produces anhydrite (Reda 1995). The decomposition calcium sulfate reagent dehydrate varies from 87 to 133 °C in comparison with 100 °C for the decomposition of water and produce soluble anhydrite, rather than the insoluble anhydrite, or hemihydrate (Elprince et al. 1982). By maintaining the samples at 70 °C for 45 min., and later at 135–150 °C for 15 min., we derived an estimate of the percentage of crystal water weight loss for this temperature

interval, referred to as the weight of the dry sample at 70 °C. The recovery percentage for this temperature interval was 19.66.

Checking the fit of the proposed OMRAN GypSim method

A formal accuracy assessment involves field verification of the proposed model was performed following the procedures of Congalton and Green (1999). From a statistical perspective, the number of samples to be validated must be adequate for measuring the variability associated with the variable tested. Several approaches were proposed for testing how well the proposed model fits the data. Most approaches rely on the idea of comparing an observed number of individuals with the number expected if the fitted model were valid. These observed and expected numbers are combined to form a Chi square statistic called the goodness of fit. The model was utilized to predict gypsum values based on soil properties. Then, regressions were developed between predicted values and actual gypsum (measured in the laboratory) to evaluate the accuracy of the model.

The interlaboratory study was accomplished to measure the accuracy (reproducibility and repeatability) of the proposed method. Repeatability is a measure repeats some number within each laboratory by the same operator and equipment, which should yield the best smallest variation among readings. Reproducibility is a measure to perform the test method in many different laboratories on the same material. Because we now have different operators, different equipment, and different environmental conditions, we should expect to have greater variability in the results from different laboratories. Repeatability and reproducibility variation are best computed as a standard deviation.

Results and discussion

Natural and reagent gypsum transformation

Table 1 shows the results obtained for water loss associated with gypsum transformation from reconstituted gypsum samples upon drying at 105 °C for 24 h. The determined values for crystal water percentage lost upon drying using natural and reagent gypsum appear to be closed, which indicate gypsum transformation to bassanite and anhydrite has very little variations in the composition. Percentage of hygroscopic water for the non-gypsiferous sandy and clay soils were 0.27 and 8.74%, respectively. Percentage of hygroscopic water for the natural pure gypsum and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reagents were 4.24 and 3.64%, respectively.

Table 1 Gypsum determination using silica-gel and acetone methods compared to the proposed method in synthetic samples

Added gypsum %	Clay soils					Sandy soils				
	Silica-gel method			Acetone method	Proposed method	Silica-gel method			Acetone method	Proposed method
	Hygr. water %	Cryst. water %	Silica-gel			Hygr. water %	Cryst. water %	Silica-gel		
CaSO ₄ · 2H ₂ O										
0	8.74	—	—	—	—	0.27	—	—	—	—
5	8.50	1.06	5.27	4.80	5.18	0.98	1.04	5.16	4.88	5.09
10	8.47	2.12	10.53	9.48	10.37	0.64	2.07	10.29	9.41	10.12
15	8.21	3.22	16.00	14.32	15.75	0.81	3.10	15.42	14.36	15.16
20	7.83	4.19	20.81	19.20	20.49	0.98	4.13	20.56	19.25	20.20
25	7.72	5.20	25.84	24.11	25.43	1.15	5.20	25.88	24.26	25.43
30	7.38	6.23	30.96	29.15	30.46	1.31	6.31	31.06	29.14	30.86
35	7.08	7.27	36.16	34.12	35.55	1.47	7.24	35.98	34.28	35.40
40	6.90	8.29	41.20	39.13	40.54	1.64	8.25	41.03	38.80	40.34
45	6.52	9.32	46.31	44.06	45.57	1.80	9.28	46.12	43.72	45.38
50	6.17	10.41	51.73	48.91	50.90	1.96	10.32	51.29	48.72	50.46
55	5.96	11.93	56.82	53.80	58.34	2.12	11.42	56.77	53.60	55.84
60	5.72	12.33	61.28	59.32	60.29	2.28	12.42	61.74	58.41	60.73
65	5.50	13.38	66.51	63.73	65.43	2.45	13.44	66.80	63.88	65.72
70	5.22	14.46	71.86	68.25	70.71	2.61	14.46	71.86	68.21	70.71
75	5.00	15.44	76.74	74.00	75.50	2.78	15.48	76.94	73.78	75.70
80	4.70	16.45	81.85	78.92	80.44	2.94	16.54	82.25	78.97	80.88
85	4.43	17.45	86.74	83.76	85.33	3.10	17.48	86.88	84.12	85.48
90	4.17	18.44	91.65	88.80	90.17	3.11	18.57	92.32	88.92	90.81
95	3.90	19.31	95.97	93.76	94.43	3.47	19.34	96.17	93.83	94.57
100	3.64	20.12	101.78	98.15	98.39	3.64	20.12	102.00	98.12	98.39
Natural gypsum										
0	8.74	—	—	—	—	0.27	—	—	—	—
5	8.60	1.00	5.20	4.87	5.10	0.49	1.00	5.19	4.80	5.09
10	8.49	2.03	10.48	9.56	10.35	0.70	2.00	10.33	9.66	10.17
15	8.14	3.06	15.82	14.27	15.61	0.81	3.01	15.51	14.47	15.31
20	7.92	3.98	20.57	19.44	20.30	1.02	3.99	20.60	19.38	20.30
25	7.80	5.02	25.89	24.62	25.60	1.23	5.05	26.04	24.50	25.69
30	7.55	5.98	30.84	29.03	30.50	1.50	5.98	30.88	29.32	30.42
35	7.25	6.96	35.91	33.81	35.50	1.59	6.99	36.07	34.29	35.55
40	7.08	7.95	41.03	38.82	40.55	1.76	7.98	41.14	38.85	40.59
45	6.84	8.94	46.13	44.02	45.59	2.00	8.95	46.19	43.62	45.52
50	6.40	10.04	51.82	48.90	51.20	2.19	9.95	51.34	48.80	50.61
55	6.36	11.00	56.79	53.69	56.10	2.35	10.98	56.64	53.73	55.85
60	6.12	11.91	61.43	58.56	60.74	2.68	11.96	61.73	58.42	60.83
65	5.88	12.98	66.98	64.35	66.20	2.87	12.95	66.80	63.63	65.87
70	5.65	13.89	71.68	68.60	70.84	3.12	13.89	71.66	68.43	70.65
75	5.31	14.92	76.93	73.38	76.09	3.24	14.90	76.87	73.36	75.79
80	5.02	15.98	82.42	78.26	81.50	3.40	15.89	81.97	78.21	80.82
85	4.74	16.75	86.39	83.60	85.43	3.63	16.84	86.86	83.84	85.66
90	4.52	17.79	91.75	88.32	90.73	3.72	17.81	91.85	88.70	90.59
95	4.47	18.58	95.83	90.18	94.76	4.10	18.51	95.94	93.75	94.15
100	4.24	19.39	101.89	92.78	98.89	4.24	19.39	101.58	98.48	98.63

Table 2 Gypsum content as determined by acetone, silica-gel methods compared with the proposed method

Soil no.	Soil separates, %			Hygroscopic water, %	Silica-gel method			Gypsum, % acetone	Gypsum, %	
	Sand	Silt	Clay		Crystal water, %	Moisture content	Gypsum, %		Proposed method	Regression equation
1	83.00	5.00	12.00	2.30	0.75	3.05	3.86	3.40	3.81	4.14
2	39.40	30.00	30.60	6.45	2.61	9.06	13.46	13.23	13.28	13.61
3	89.20	7.20	3.60	1.20	4.65	5.85	23.98	22.32	23.65	23.52
4	90.00	6.50	3.50	0.58	0.20	0.78	1.03	0.93	1.02	1.37
5	84.00	10.20	5.80	1.95	4.55	6.50	23.46	22.70	23.14	23.19
6	81.10	10.30	8.60	1.72	3.34	5.06	17.22	15.13	16.99	16.90
7	69.50	11.50	19.00	3.60	0.17	3.77	0.88	0.57	0.86	1.29
8	30.50	38.50	31.00	6.32	1.04	7.36	5.36	4.26	5.29	5.79
9	93.00	5.20	1.80	0.72	2.59	3.31	13.35	12.21	13.17	13.32
10	20.00	21.80	58.20	11.59	0.81	12.40	4.17	4.12	4.12	4.78
11	91.20	3.60	5.20	1.65	3.40	4.75	15.98	15.23	17.29	17.44
12	83.00	8.40	8.60	2.32	5.33	7.65	27.48	25.83	27.11	26.96
13	44.20	34.60	29.20	4.80	3.56	8.36	18.36	16.88	18.11	17.66
14	24.00	21.00	55.00	11.92	4.97	16.89	25.63	25.43	25.28	25.65
15	3.00	29.00	52.00	11.42	4.73	16.15	24.39	24.87	24.06	24.49
16	90.40	5.60	4.00	0.78	0.40	1.18	2.06	2.10	2.03	2.40
17	76.40	17.30	6.30	1.30	1.60	2.90	8.25	7.82	8.14	8.34
18	78.80	15.20	6.00	1.28	1.48	2.76	7.63	7.21	7.53	7.77
19	90.30	6.60	3.10	0.58	0.68	1.26	3.51	3.12	3.46	3.76
20	74.00	20.20	5.80	1.05	1.23	2.28	6.34	5.00	6.26	6.45
21	29.20	38.20	32.60	6.94	2.73	9.67	14.07	13.80	13.89	14.25
22	83.20	5.60	11.20	2.36	1.78	4.14	9.17	8.56	9.05	9.30
23	77.20	9.30	13.50	2.67	1.93	4.60	9.95	8.78	9.82	9.98
24	86.00	11.50	2.50	0.43	0.31	0.74	1.60	1.53	1.58	1.92
25	69.90	9.50	20.60	3.84	0.16	4.00	0.83	0.63	0.81	1.22
26	74.20	8.60	17.00	3.88	2.60	6.48	13.40	13.82	13.22	13.53
27	80.00	10.20	9.80	3.22	6.70	9.92	34.55	33.63	34.08	34.00
28	89.80	6.00	4.20	1.18	3.16	4.34	16.29	16.40	16.07	16.14
29	85.20	13.20	1.60	1.66	6.71	8.37	34.61	32.52	34.13	34.03
30	12.00	25.00	53.00	12.61	1.04	13.65	5.35	5.10	5.29	6.79
31	13.00	27.00	60.00	12.14	0.98	13.12	5.05	4.62	4.98	5.71
32	30.00	22.00	48.00	9.57	1.00	10.57	5.15	4.20	5.09	5.65
33	12.00	40.00	48.00	9.58	1.05	10.63	5.42	4.30	5.34	5.90
34	83.00	9.60	7.40	1.39	0.20	1.59	1.03	0.80	1.02	1.41
35	62.50	21.00	16.50	3.30	0.75	4.05	3.86	3.72	3.81	4.21
36	70.00	10.60	19.40	3.82	0.51	4.33	2.63	2.43	2.59	3.03
37	62.00	15.50	22.50	4.72	2.04	6.76	10.52	9.32	10.38	10.70
38	84.90	4.50	10.60	1.97	2.43	4.40	12.53	10.12	12.36	12.37
39	80.50	5.30	14.20	2.86	1.55	4.41	7.99	7.32	7.88	8.14
40	84.50	8.30	7.20	1.36	0.57	1.93	2.93	2.65	2.90	3.23
41	25.50	32.50	42.00	8.44	1.16	9.60	5.98	6.24	5.90	6.43
42	86.50	7.30	6.20	1.84	6.36	8.20	32.80	31.73	32.35	32.01
43	78.00	8.50	13.50	2.86	2.45	5.31	12.63	11.22	12.46	12.63
44	88.00	6.40	5.60	1.63	3.58	5.21	18.46	17.40	18.21	18.29
45	70.00	12.20	17.80	3.91	3.34	7.25	17.22	15.48	16.99	17.12
46	86.50	6.30	7.20	1.80	2.80	4.60	14.44	13.82	14.24	14.39

Table 2 continued

Soil no.	Soil separates, %			Hygroscopic water, %	Silica-gel method			Gypsum, % acetone	Gypsum, %	
	Sand	Silt	Clay		Crystal water, %	Moisture content	Gypsum, %		Proposed method	Regression equation
47	48.40	25.20	26.40	5.17	0.76	5.93	3.92	3.28	3.87	4.28
48	89.30	6.80	3.90	0.73	1.91	2.64	9.85	8.46	9.72	9.81
49	88.40	6.60	5.00	1.02	0.72	1.74	3.71	3.62	3.66	4.00
50	87.50	9.50	3.00	0.52	0.38	0.90	1.95	1.73	1.93	2.27
51	91.70	6.20	2.10	0.36	0.22	0.58	1.13	1.03	1.12	1.48
52	68.90	22.50	8.60	2.12	3.98	6.10	20.52	19.80	20.24	20.23
53	75.30	10.20	14.50	4.24	7.77	12.01	40.17	38.48	39.52	39.33
54	24.00	30.40	45.60	9.32	1.32	10.64	6.80	6.43	6.71	7.31
55	20.90	26.80	52.30	11.18	3.30	14.48	17.01	16.70	16.79	17.33
56	23.30	40.70	36.00	7.45	2.02	9.47	10.41	10.12	10.27	10.71
57	30.50	34.30	35.20	7.03	1.14	8.17	5.87	5.22	5.80	6.26
58	71.10	15.30	13.60	1.75	3.36	5.09	17.28	15.20	16.99	16.60
59	54.00	25.20	20.80	1.01	1.26	2.22	6.39	5.00	6.26	5.35
60	80.30	9.80	9.90	0.72	1.90	2.60	9.80	8.58	9.72	9.26
Soil no.	Soil separates, %			Hygroscopic water, %	Silica-gel method			Gypsum, % acetone	Gypsum, %	
	Sand	Silt	Clay		Crystal water, %	Moisture content	Gypsum, %		Proposed method	Regression equation
61	89.40	6.90	3.70	0.53	0.23	0.76	1.08	0.97	1.17	1.47
62	80.50	10.70	8.80	1.67	3.37	5.04	17.27	15.17	17.14	17.01
63	29.90	38.90	31.20	6.27	1.07	7.34	5.41	4.30	5.44	5.90
64	90.60	4.00	5.40	1.60	3.43	5.03	16.03	15.27	17.45	17.55
65	43.60	35.00	29.40	4.75	3.59	8.34	18.41	16.92	18.26	17.77
66	38.80	30.40	30.80	6.40	2.64	9.04	13.51	13.27	13.43	13.72
67	83.40	10.60	6.00	1.90	4.58	6.48	23.51	22.74	23.30	23.29
68	89.80	6.00	4.20	0.73	0.43	1.16	2.11	2.14	2.19	2.51
69	29.40	22.40	48.20	9.52	1.03	10.55	5.20	4.24	5.24	5.76
70	23.40	21.40	55.20	11.87	5.00	16.87	25.68	25.47	25.43	25.76
71	2.40	29.40	52.20	11.37	4.76	16.13	24.44	24.91	24.21	24.60
72	92.40	5.60	2.00	0.67	2.62	3.29	13.40	12.25	13.33	13.43
73	19.40	22.20	58.40	11.54	0.84	12.38	4.22	4.16	4.27	4.88
74	82.40	8.80	8.80	2.27	5.36	7.63	27.53	25.87	27.26	27.07
75	90.00	6.70	3.30	1.15	4.68	5.83	24.03	22.36	23.80	23.67
76	83.80	4.50	11.70	2.25	0.78	3.03	3.83	3.42	3.97	4.29
77	13.80	26.50	59.70	12.09	1.01	13.10	5.02	4.64	5.14	5.86
78	82.70	5.80	11.50	2.31	1.81	4.12	9.14	8.58	9.21	9.40
79	77.20	16.80	6.00	1.25	1.63	2.88	8.22	7.84	8.29	8.49
80	78.00	8.80	13.20	2.69	1.91	4.60	9.92	8.80	9.72	9.92
81	70.70	9.00	20.30	3.86	0.14	4.00	0.80	0.65	0.71	1.15
82	79.60	14.70	5.70	1.30	1.46	2.76	7.60	7.23	7.43	7.70
83	91.10	6.10	2.80	0.60	0.66	1.26	3.48	3.14	3.36	3.69
84	86.00	12.70	1.30	1.68	6.69	8.37	34.58	32.54	34.03	33.96
85	12.80	24.50	52.70	12.63	1.02	13.65	5.32	5.12	5.19	6.73
86	86.80	11.00	2.20	0.45	0.29	0.74	1.57	1.55	1.48	1.86
87	92.50	5.70	1.80	0.38	0.20	0.58	1.10	1.05	1.02	1.42
88	12.80	39.50	47.70	9.60	1.03	10.63	5.39	4.32	5.24	5.83
89	61.50	15.70	22.80	4.74	2.02	6.76	10.49	9.34	10.27	10.59

Table 2 continued

Soil no.	Soil separates, %			Hygroscopic water, %	Silica-gel method			Gypsum, % acetone	Gypsum, %	
	Sand	Silt	Clay		Crystal water, %	Moisture content	Gypsum, %		Proposed method	Regression equation
90	83.80	9.10	7.10	1.41	0.18	1.59	1.00	0.82	0.92	1.34
91	28.70	38.40	32.90	6.96	2.71	9.67	14.04	13.82	13.78	14.14
92	70.30	11.00	18.70	3.62	0.15	3.77	0.85	0.59	0.76	1.22
93	73.70	8.80	17.30	3.90	2.58	6.48	13.37	13.84	13.12	13.42
94	24.80	29.90	45.30	9.34	1.30	10.64	6.84	6.46	6.61	7.24
95	89.30	6.20	4.50	1.20	3.14	4.34	16.33	16.43	15.97	16.02
96	62.00	21.20	16.80	3.32	0.73	4.05	3.90	3.75	3.71	4.10
97	69.50	10.80	19.70	3.84	0.49	4.33	2.67	2.46	2.49	2.91
98	87.00	9.70	3.30	0.54	0.36	0.90	1.99	1.76	1.83	2.15
99	68.40	22.70	8.90	2.13	3.97	6.10	20.56	19.83	20.19	20.16
100	25.00	32.70	42.30	8.45	1.15	9.60	6.02	6.27	5.85	6.36
101	74.80	10.40	14.80	4.25	7.76	12.01	40.21	38.51	39.47	39.26
102	20.40	27.00	52.60	11.19	3.29	14.48	17.05	16.73	16.73	17.26
103	22.80	40.90	36.30	7.46	2.01	9.47	10.45	10.15	10.22	10.64
104	79.50	10.40	10.10	3.23	6.69	9.92	34.59	33.66	34.03	33.93
105	74.80	19.70	5.50	1.06	1.22	2.28	6.38	5.03	6.21	6.43
106	71.50	15.20	13.30	1.76	3.35	5.11	17.32	15.23	16.99	16.58
107	87.50	6.60	5.90	1.64	3.57	5.21	18.50	17.43	18.16	18.22
108	69.50	12.40	18.10	3.92	3.33	7.25	17.26	15.51	16.94	17.05
109	80.00	5.50	14.50	2.87	1.54	4.41	8.03	7.35	7.83	8.07
110	89.70	6.70	3.60	0.74	1.90	2.64	9.89	8.49	9.66	9.79
111	80.70	9.70	9.60	0.73	1.89	2.62	9.76	8.55	9.72	9.24
112	84.90	8.20	6.90	1.37	0.56	1.93	2.89	2.62	2.85	3.21
113	86.90	7.20	5.90	1.85	6.35	8.20	32.76	31.70	32.30	31.99
114	78.40	8.40	13.20	2.87	2.44	5.31	12.59	11.19	12.41	12.61
115	54.40	25.10	20.50	0.98	1.24	2.22	6.35	4.97	6.26	5.26
116	30.90	34.20	34.90	7.00	1.12	8.12	5.83	5.24	5.70	6.17
117	86.90	6.20	6.90	1.77	2.78	4.55	14.40	13.79	14.14	14.31
118	87.90	6.80	5.30	0.99	0.70	1.69	3.67	3.59	3.56	3.86
119	85.30	4.40	10.30	1.94	2.41	4.35	12.49	10.09	12.26	12.28
120	48.80	25.10	26.10	5.14	0.74	5.88	3.88	3.25	3.76	4.20

It appears from the results that gypsum transformation to bassanite and anhydrite show very little variations in the composition of gypsum. The difference is mainly in its chemical composition as a result of its dehydration upon heating. Crystal water of natural gypsum and reagent used is constitutes 19.39 and 20.12% of the total weight, respectively. This means that gypsum decomposes upon heating to bassanite and finally to anhydrite, loss average 19.76% of its total weight.

Gypsum content determination in soil samples

To test the validity of Eq. 1, results from the silica-gel, acetone, and the proposed method were compared

(Table 2) for 120 samples. Regression equation (Eq. 2) indicated that the calculated values are highly correlated and overestimation of gypsum content compared with acetone method, whereas underestimation compared with silica-gel method. With this closed agreement, we suggest that this equation could be used with good accuracy for predicting gypsum content in soils.

$$Y = -0.3008 + 4.919X_1 + 0.5566X_2 - 0.0724X_3.$$

(2)

where, Y = Gypsum content, X_1 = Crystal water, X_2 = Hygroscopic water, X_3 = Clay content.

The results indicate that percent total water loss associated with drying gypsiferous soil samples is not only

Fig. 2 Gypsum content determined from precipitated BaSO_4 as related to gypsum content from the proposed method and accuracy of proposed method compared with other methods

Table 3 Recovery of known pure gypsum amount added to soil by silica-gel, acetone, and the proposed method

Gypsum, %	Proposed		Silica-gel		Acetone	
	Mean	SD	Mean	SD	Mean	SD
5	5.14	0.06	6.04	0.31	4.04	0.43
10	10.06	0.06	10.96	0.31	8.96	0.43
20	20.25	0.05	21.15	0.30	19.15	0.42
30	30.78	0.08	31.68	0.33	29.68	0.45
40	40.42	0.08	41.32	0.33	39.32	0.45
50	50.63	0.17	51.53	0.42	49.53	0.54
60	60.72	0.02	61.62	0.27	59.62	0.39
70	70.65	0.05	71.55	0.30	69.55	0.42
80	80.84	0.04	81.74	0.29	79.74	0.41
90	90.80	0.01	91.70	0.25	89.70	0.37
100	98.89	0.49	99.79	0.74	97.79	0.86

SD standard deviation

dependent on soil texture and its clay content, but also on percent gypsum. However, the rate of gypsum dehydration is catalyzed by soil matrix nature (Elprince et al. 1982). Clay minerals contain a considerable amount of crystal water. During the determination of the crystal water in gypsum by the classical thermal analysis method, not only the removal of the crystal water occurs, but also, the dehydration of the clay minerals occurs. To prevent errors

arising in the determination of the crystal water in gypsum, first, it is necessary to dry the gypsum samples to constant mass at 50 °C in an electric dryer. Crystal water of pure gypsum is about 19.76% of its total weight. This means that when gypsum decomposes upon heating to bassanite and finally to anhydrite, loses about 19.76% of its total weight. Accordingly, the properties of gypsiferous soils on an oven-dry weight basis should be corrected to include gypsum crystal water. Further, it is necessary to avoid the possible calculation error when the data are expressed on an oven-dry weight basis that the loss of gypsum crystal water must be subtracted from the total soil moisture content if determined by drying at 150 °C.

An accuracy assessment of the proposed method

Gypsum content (Fig. 2a) calculated in the proposed method was found to be highly correlated ($r^2 = 0.99$) with those determined by the gravimetry of precipitated BaSO_4 . For testing the accuracies of the Eq. 2, gypsum content is calculated for the soils (Fig. 2b) and for the artificial gypsum (Fig. 2c, d). Regression equation indicates that the calculated values overestimate the gypsum compared with added gypsum and the proposed OMRAN GypSim method.

Table 3 shows the average percentage of added gypsum retrieved by the three methods indicates that the reproducibility of the proposed method is the highest, which are

ranged between 0.01 and 0.49 (average 0.10) followed by silica-gel, which is ranged between 0.25 and 0.74 (average 0.35) then the acetone method, which is ranged between 0.37 and 0.86 (average 0.47). This simple, yet effective method determined gypsum content to within 1%, whereas other methods overestimated gypsum content by as much as 10%.

Modelling the proposed method

Statistical analysis based on Table 2 shows positive and the highly correlation between hygroscopic water and clay content. The prediction equation can be written as follows:

$$Y = (Y1 + Y2) + Y3. \quad (3)$$

where Y = total moisture content, $Y1$ and $Y2$ = hygroscopic water of soil and gypsum, respectively, $Y3$ = crystal water of gypsum.

$$Y1 = 0.1998 X1 - 0.2821 (r^2 = 0.98). \quad (4)$$

where $Y1$ = hygroscopic water of soil, $X1$ = clay content.

$$Y2 = 0.0424 X2 (r^2 = 0.93). \quad (5)$$

where $Y2$ = hygroscopic water of gypsum, $X2$ = gypsum content.

Also, there is a positive and high significant relation between gypsum content and crystal water. The stepwise equation that governs this relation can be summarized as:

$$Y3 = 0.1938 X2 - 0.0065 (r^2 = 0.99). \quad (6)$$

From the above equations, the gypsum content can be derived as follows:

$$Y = 0.1998 X1 + 0.2362 X2 - 0.2761. \quad (7)$$

where Y = total moisture content, $X1$ = clay content, $X2$ = gypsum content

$$X2 = Y - 0.1998X1 + 0.2761/0.2362. \quad (8)$$

So, Eq. 8 may be corrected by approximately 3.6% (deviate values from the standard) as follows:

$$X2 = Y - 0.1998X1 + 0.2761/0.2362 \times 0.964. \quad (9)$$

A gypsum simulation (OMRAN GypSim) model is developed and implemented for gypsum determination. The OMRAN GypSim is a tool written in the language Java and is used to calculate gypsum content in arid soils. Java is one of the most popular programming languages in use. An easy-to-use graphical user interface (GUI) has been designed for the running of the model. The GUI allows users to interact with the computer hardware in a user-friendly way. In the OMRAN GypSim menu (Fig. 3) the user selects the determination methods and the parameters,

Fig. 3 OMRAN GypSim application menu to calculate gypsum content in arid soils

that is, hygroscopic and crystal water, soil moisture, and clay content. A screenshot of the application model to calculate and display the gypsum content is shown in Fig. 3.

Benefits and advantages of the proposed OMRAN GypSim method

There will be much debate among soil scientists regarding the best or favored methods for gypsum content determination. Researchers should keep in mind the following factors when considering the best methods:

1. Cost and simplicity. The labor cost vs. capital equipment cost is one of the main considerations when choosing methods. The proposed method has very low cost.
2. Available instrumentation. The most powerful and valuable diagnosis can be done with quite simple equipment. OMRAN GypSim method has very low infrastructure expenses.
3. Accuracy and precision requirements are generally lower in other methods than in the proposed method. Accuracy costs money and the proposed method using

weighing and heating only, which is faster while still providing sufficient accuracy and precision for diagnostic and monitoring purposes. OMRAN GypSim method determined gypsum content to within 1%, whereas other methods overestimated gypsum content by as much as 10%.

4. Adaptable to various soil types. Many methods were developed for particular soil types and the calibration data may not be so relevant to other soil types. In particular, the proposed method developed and examined for different soil types (e.g., sand, clay, soil, etc.) and a wide variety of conditions (e.g., salinity, calcareous soil, alkalinity).
5. Robust and ideal for applications that require speed results and decision. The gypsum content of 120 soil samples can be determined in 60 min work.
6. An easy-to-use graphical user interface has been designed for the automation of the gypsum calculation.

Conclusions

Conventional methods of gypsum determination are time-consuming and expensive and sometimes incorporate the use of environmentally damaging chemicals. There are many proposed methods of gypsum determination and each one was reported with its own limitations. Recovery gypsum content by using acetone methods of known amount of pure gypsum added to soil shows acetone is underestimated. This could be attributed to incomplete extraction of gypsum in acetone method, then more time consuming, and degree of accuracy. These methods seem to have many limitations, which can be attributed to the degree of accuracy and slow in processing. However, the silica-gel method gives values overestimate the gypsum content, which could be attributed to the partial dehydration and dehydroxylation of clay minerals causing overestimation of gypsum content. The speed and simplicity of analysis and the accuracy of the results are the main factors, which are considered in the proposed method. OMRAN GypSim was proposed for gypsum determination in soils. The proposed method for gypsum determination determines the water loss of a soil sample by heating at 70 °C and 135–150 °C, which allows an accurate estimate of the gypsum content of a soil using a recovery factor of 19.66%. In a laboratory, the gypsum content of 120 soil samples can be determined in 60 min work. Regression equation indicated that gypsum content determined by proposing method was highly correlated in a nearly 1:1 relationship. The reproducibility of the proposed method is the highest (0.10) followed by silica-gel (0.35) then the acetone method (0.47). In conclusion, the proposed methods are simple, accurate, rapid,

and less expensive. The results of pure gypsum content, as well as recovery of gypsum from the artificial mixture, suggest that the proposed method is recommended to be used in the arid- soil regions. This method is simple, rapid and less expensive. Also, an easy-to-use graphical user interface has been designed for the running of the model. A different approach for future rapidly characterizing soil gypsum at a large scale is offered by the remote sensing technique.

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