JOURNAL OF AGRICULTURE AND APPLIED BIOLOGY
2023, Vol. 4, No. 2, 182 - 190
http://dx.doi.org/10.11594/jaab.04.02.08
E-ISSN: 2723-5106

Research Article

Comparison between two gypsum content determination methods applied to the study of soils in arid regions

Fouzia Youcef[1, 2*], Djihane Kairouani[2], Fatiha Boukarkar[2], Baelhadj Hamdi Aïssa[1, 2]

[1]University of KASDI Merbah-Ouargla, Laboratory of Biogeochemistry of Desertic Areas, Ouargla 30 000 Algeria
[2]University of KASDI Merbah-Ouargla, Faculty of Science of Nature and Life, Ouargla 30 000 Algeria

Article history:

Submitted 31 October 2023
Accepted 18 November 2023
Published 6 December 2023

Keywords:

Arid region
Artieda method
Precipitated $BaSO_4$ method
Thermogravimetry
Weight loss

***Corresponding author:**

E-mail:
youcef_yf@yahoo.fr

Abstract

With the scarcity, degradation of soils, the growing populations and the need to guarantee their food security, the valorization of gypsum soils widespread in arid and semi-arid regions is becoming a necessity. North African countries have a large part of their land area located in arid regions. It is therefore important to characterize the gypsum content using simple, rapid, economical and, environmentally friendly methods. Several methods have been proposed in the literature (chemical, thermogravimetric, and x-ray techniques). In this work, a comparison between two methods for gypsum determination in soils was undertaken. The first method of Coutinet is chemical and based on the use of $BaSO_4$ for the precipitation of sulfate ions. The second method is Artieda method which is based on measuring the weight difference caused by the loss of crystalline water from gypsum molecules between the temperatures of 70 and 90 °C. To achieve the objective of this work, forty-three soil samples were analyzed. They were taken from two arid regions (Ouargla and Touggourt) located in the northern Sahara (Algeria). The soils contain gypsum accumulations. The results showed that most of the samples are slightly gypsiferous, with 36 and 32 samples for the Coutinet and Artieda methods respectively. A strong positive correlation (R^2 = 0.95) exists between the results of the two methods studied. For gypsum contents higher than 2 %, the correlation coefficient is 0.94. However, for samples with contents less than 2 %, the correlation is very weak with R^2=0.19. The Artieda method is thus encouraged for the gypsum quantification in soils of arid regions. This method is easy, requiring simple laboratory equipment (mainly a ventilated oven and a precision balance). Chemical methods have the disadvantage of being time-consuming and using expensive chemicals that are dangerous for the environment and human health.

How to cite:
Youcef, F., Kairouani, D., Boukarkar, F., & Hamdi Aïssa, B. (2023). Comparison between two gypsum content determination methods applied to the study of soils in arid regions. *Journal of Agriculture and Applied Biology, 4*(2): 182 - 190. doi: 10.11594/jaab.04.02.08

1. Introduction

Gypsum is very common in soils of arid and semi-arid regions. This sedimentary rock is formed of hydrated calcium sulfate ($CaSO_4$. $2H_2O$). Casby-Horton et al. (2015) found that gypsum contents greater than 30 % have a significant impact on the physical and chemical properties that are important for agronomic purposes. However, according to Escudero et al. (2015) even low soil gypsum concentrations have noticeable impacts on plants. Future agricultural demands due to population growth and economic development have put more strain on soils globally, even on those that were previously thought to be marginal due to their high gypsum content (Casby-Horton et al., 2015; Herrero et al., 2020; Herrero & Zartman, 2021). When compared to other types of soils, those containing gypsum have not been thoroughly studied (Álvarez et al., 2022). Among these studies, we can cite: Hamdi-Aïssa (2001), Youcef et al. (2014), Youcef (2016), Moret-Fernández and Herrero (2015), Abdesselam and Timechbache (2016), Poch et al. (2021), Hassan (2021), and Al-Kayssi (2022). Therefore, the study and characterization of gypsiferous soils and the development of precise, economic, rapid and environmentally friendly methods for estimating the gypsum content in the soil become a necessity.

The amount of gypsum in the soil can be quantified using a variety of techniques, though not all of them are equally precise. Moreover, the expenses and duration of these differ significantly (Álvarez et al., 2022). These techniques can be grouped into three categories: x-ray techniques, thermogravimetric techniques, and wet chemical techniques (Lebron et al., 2009). Some methods are economic, using only simple laboratory equipment such as that of Artieda et al. (2006) and Lebron et al. (2009) while others are long and require the use of many chemical products such as the method of Coutinet (1965). According to Artieda et al. (2006), it is lengthy and laborious to determine the gypsum content of soil using methods that rely on SO_4 determination. Furthermore, because these techniques do not precisely titrate gypsum, errors may result from the presence of other sulfate minerals. According to Omran (2016), conventional techniques for determining gypsum are expensive, time-consuming, and sometimes involve the use of chemicals that are harmful to the environment.

The acetone method is based on completely dissolving the gypsum in the sample and then reprecipitating it with the addition of acetone. It is necessary to fully dissolve the precipitate again and measure the amount of sulphates in the solution (Álvarez et al., 2022). The reactivity of the acetone-based methods with sulfates that do not originate from gypsum is a disadvantage (Herrero et al., 2016).

In the method of Coutinet (1965), gypsum is dissolved by ammonium carbonate, and precipitated in the form of sulfate by barium chloride. This method is applicable to all gypsum contents.

For the majority of soils and other heterogeneous gypsum-rich materials, wet chemistry methods for quantifying the gypsum content are inappropriate (Herrero et al., 2016). However, the thermogravimetric characteristics of gypsum make it possible to quickly and easily determine its content with enough accuracy for a variety of pedagogical purposes (Artieda et al., 2006). Lebron et al. (2009) have developed a more precise, simple, and improved method for quantifying soil's gypsum content. This approach takes into account the variations in water content between bassanite and gypsum after an oven heating of samples at 105°C. Regardless of the type of clay mineralogy present, the real amount of gypsum in the sample was consistently estimated to be greater than 1 % in the absence of hydrated salts.

For gypsum contents greater than 2 %, the Artieda et al. (2006) method gives satisfactory results based on weight loss between 70 and 90 °C. The authors, however, warned against causing an overestimation if the sample contains smectite. According to Weindorf et al. (2013), modern portable X-ray fluorescence (pXRF) has a great potential for accurately estimating the amount of gypsum present in soil samples. Omran (2016) proposed a speed and simple method "OMRAN GypSim method", developing and examining different soil types and a wide variety of soil conditions. It is possible to determine the gypsum content of 120 soil samples in 60 minutes of work.

In this study, a comparison between two methods of gypsum quantification in soils applied to soil samples taken from two arid regions of south-eastern Algeria (Ouargla and Touggourt) was undertaken. The methods are: the chemical method of Coutinet (1965) and the method of Artieda et al. (2006) based on measuring the loss of gypsum constitutional water.

2 Materials and methods

2.1 Study area

This work was carried out using soil samples taken from the two regions of Ouargla and Touggourt (South East of Algeria). Ouargla region is one of the main oases of the Algerian Sahara. It is located in the Algerian Lower Sahara occupying the center of an endorheic basin. It corresponds to the lower fossil valley of Oued Mya which drains the northern slope of the Tademaït plateau and ends at Sebkha Safioune 20 km north of Ouargla. The main geomorphological groups of Ouargla region are: plateau, glacis, Chotts, Sebkha and sand dunes.

The climate of Ouargla region is hyper-arid and very dry. According to data from the National Meteorological Office (2011-2020), the average annual temperature of Ouargla is 23.7 °C, the minimum temperature of the coldest month is recorded in January with 4.58 °C, and the maximum temperature of the hottest month is recorded in July with 43.99 °C. The annual precipitation is 30.66 mm/year.

The gypsum soils in Ouargla region are found in the eastern part (at the edges of the chotts and sebkhas) and the southern part (plateau) of Ouargla basin. Touggourt is located 160 km northeast of Ouargla and 660 km southeast of Algiers. Capital of Oued Righ, Touggourt is one of the largest cities in the Algerian Sahara. The Oued Righ region belongs to the Saharan platform. This region is known as lower Sahara, because of its low altitude, particularly in the Chotts zone in the North, where altitudes are below sea level. The climate of the Touggourt region is hyperarid. The average annual temperature in the Touggourt region is 22.36 °C (Period: 2007-2016). Concerning the maximum temperature, the highest value is reached in July with 42.76 °C while the minimum temperature of the coldest month (January) is equal to 4.1 °C. The annual precipitation in the study region is 53.8 mm. The soils of the Touggourt region contain high proportions of gypsum. The main reason for this accumulation in soils is due to the precipitation of gypsum from salts contained in the aquifer and in runoff water (Samia et al., 2023).

2.2 Samples and analytical methods

A total of forty-three soil samples were studied in this work. They were taken from the regions of Ouargla and Touggourt. In this work, two methods have been adopted for the dosage of gypsum. The method of Coutinet (1965) consisting of the measure of the gypsum content after its decomposition with ammonium carbonate (5 %). The sulfate ion is released and precipitated with hot barium chloride (10 %). This method is applicable to all gypsum contents. The gypsum content is measured on the earth passed through a 100 µm sieve. The steps of the method are as follows: Weigh 5 g into a 300 mL Erlenmeyer flask. Add 100 mL of a 5 % ammonium carbonate solution and heat for fifteen minutes to boiling. Filter, and then wash the filter paper with boiling water. Acidify the filtrate with hydrochloric acid, and when boiling, precipitate with a boiling 10 % barium chloride solution. Let the solution sit, then, filter through ash-free filter paper, wash with boiling water until the Cl^- ions are eliminated, dry and calcine at 900 °C.

P is the weight in milligrams of SO_4Ba. The gypsum content (‰) is calculated as follows:

$$t = p \times 0.147 \quad \text{......................Eq. 1.}$$

In the method of Artieda et al. (2006), we used a ventilated oven for drying the samples, to obtain thermal homogeneity. The steps of this method are as follows:

A tared Pyrex crystallizing dish was filled with 10 to 20 g of air-dried soil (< 2 mm), and the weight was recorded to the closest 0.001 g. The crystallizing dish was transferred to an oven at 70 °C until a constant weight was obtained, then it was kept in an oven at 90 °C until its weight remained constant. The constant weight at 70 °C will be obtained after 3 days. This time depends on the oven's volume and the number of samples. At 90 °C the time is 48 hours.

The samples were taken out of the oven and cooled completely in a desiccator before being weighed Artieda et al. (2006). The percentage of gypsum in the sample was calculated by the following formula:

$$\text{Gypsum \%} = \left(\frac{ws-wf}{ws-wt}\right) 100 \left(\frac{100}{14.95}\right) = \left(\frac{ws-wf}{ws-wt}\right) 669 \text{.......................... Eq. 2}$$

Where:

- Ws: sample weight after drying at 70 °C + Pyrex crystallizing dish;
- Wf: sample weight after drying at 90 °C +Pyrex crystallizing dish;
- wt is weight of the Pyrex crystallizing dish;
- 14.95: recovery factor of gypsum between 70 and 90 °C.

In this study, a Bruker S1 TITAN 200 Handheld XRF analyser was used for the determination of the concentrations of Ag, V, P, S, Mg, Al, Si, Ti, Cr, Mn, Ni, Fe, Pd, Zr and Cu for the soil samples studied. The results represent the average of three scans of each sample.

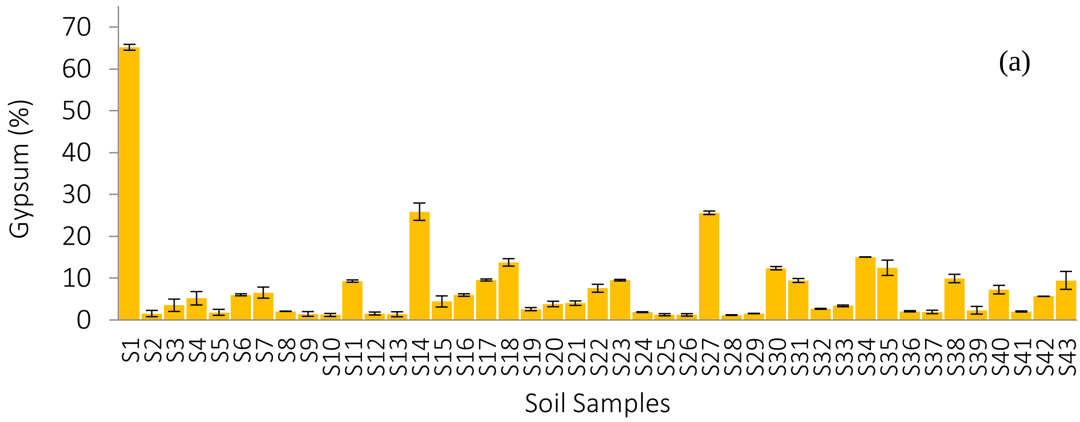
3 Results and discussion

3.1 Gypsum content of the soil samples studied

The rate of gypsum in the samples studied is variable, from 1.17 % to 65.16 % for the chemical method and from 0.05 % to 69.68 % for the Artieda method. Figure 1(a and b) presents the results of the gypsum contents using the Coutinet method (a) and the Artieda method (b). It shows that the samples studied mainly belong to the class of slightly gypsiferous soils with 36 and 32 samples for the Coutinet and Artieda methods respectively.

These gypsum contents in the samples studied are explained by the presence of different forms of gypsum accumulations such as: crusts, nodules and rhizoliths. Figure 2 (a, b, and c) shows some studied soil samples, observed by the binocular. We can observe gypsum crystals with sand particles in variable dimensions and sometimes even the predominance of these crystals compared to other soil constituents (Figure 2, b).

Ouargla and Touggourt are arid regions, characterized by very significant evaporation of 2912.17 and 2335.74 mm/year respectively and very low precipitations of 30.66 and 53.8 mm/year respectively, leading to the formation of the different forms of gypsum accumulations and also to their preservation in the soil. Indeed, several studies have shown the predominance of gypsum in these two regions (Dutil, 1971; Hamdi-Aïssa, 2001; Boumaaraf, 2013; Youcef & Hamdi-Aïssa, 2014; Youcef et al., 2014; Youcef, 2016; Samia et al., 2023). According to Dutil (1971), in the northern Sahara, gypsum accumulations (crusts and "encroûtements") can only reflect dry periods where gypsum precipitated in large quantities, interspersed with wet periods where the water table level can rise.



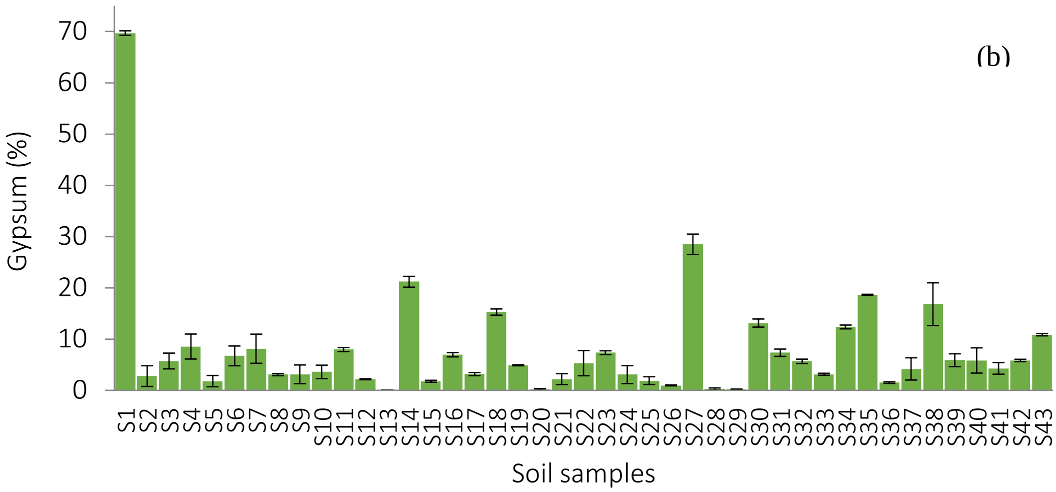


Figure1. Gypsum content of samples studied by the Coutinet method (a) and the Artieda method (b)

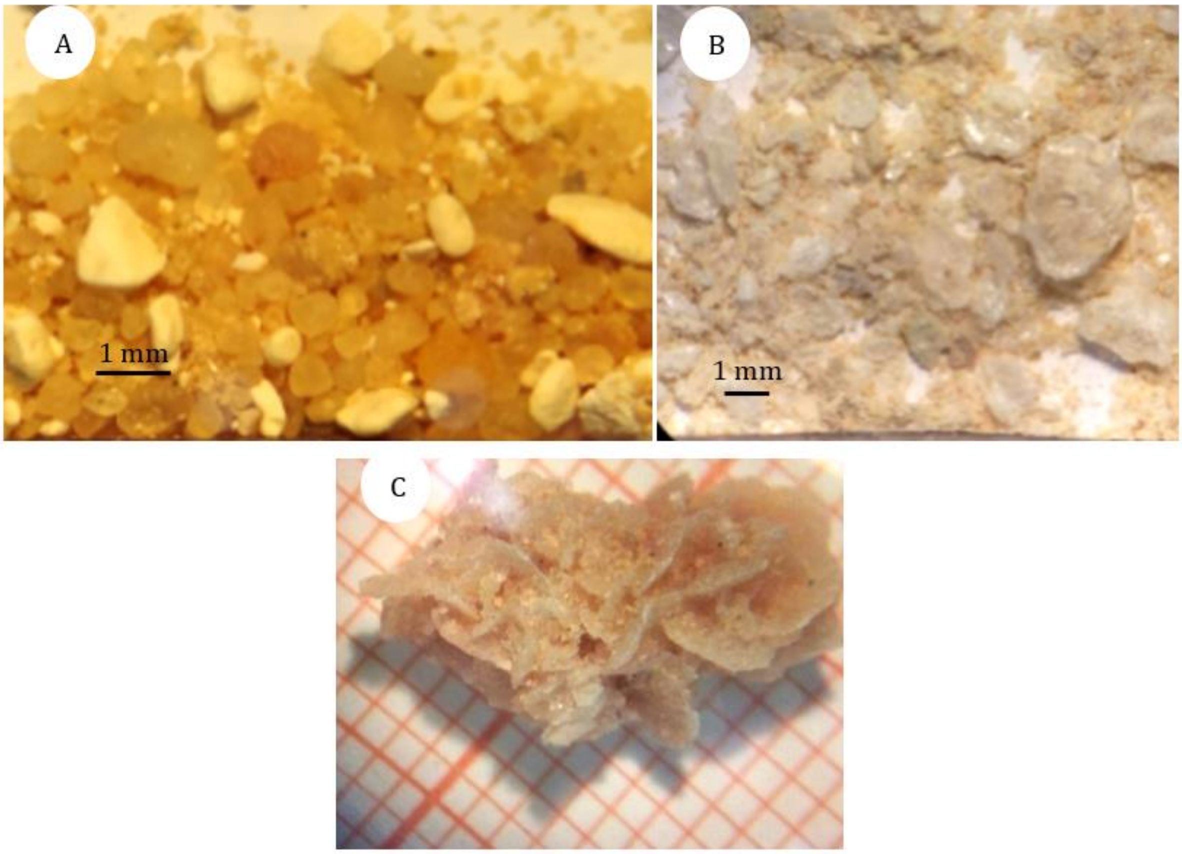


Figure 2. Some soil samples and gypsum accumulations observed with a binocular. A and B: Gypsiferous soils. C: Gypsum rosette

3.2 X-ray fluorescence results (pXRF)

The pXRF results of some samples are presented in Figure 3. Only the elements Si, S, Fe, Mg and Al presenting fairly high levels have been presented. The most dominant element is Si with percentages ranging from 62.31 to 91.74 %. Sulfur content ranges from 11.89 to 28.99 %. We also observe the presence of: Al, Mg and Fe. The other elements (Cu, Zr, Pd, Ni, Mn, Cr, Ti, P, V and Ag) present very low amounts. These results can be explained by the fact that Si is the main component of sand. The sulfur results are confirmed by the gypsum contents measured for the samples studied.

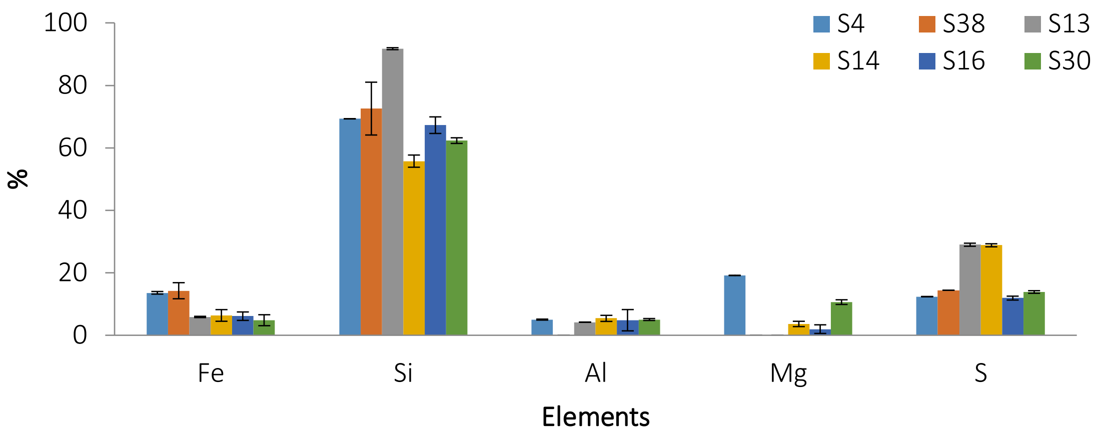


Figure 3. Principal mineral elements (Fe, Si, Al, Mg and S) measured by pXRF in some samples studied in (%)

3.3 Correlation between the results of the gypsum determination methods used

The correlation between the results of gypsum quantification by the methods of Artieda and Coutinet is presentedin Figure 4. According to the results obtained, these two methods are positively correlated with a correlation coefficient R^2=0.95.

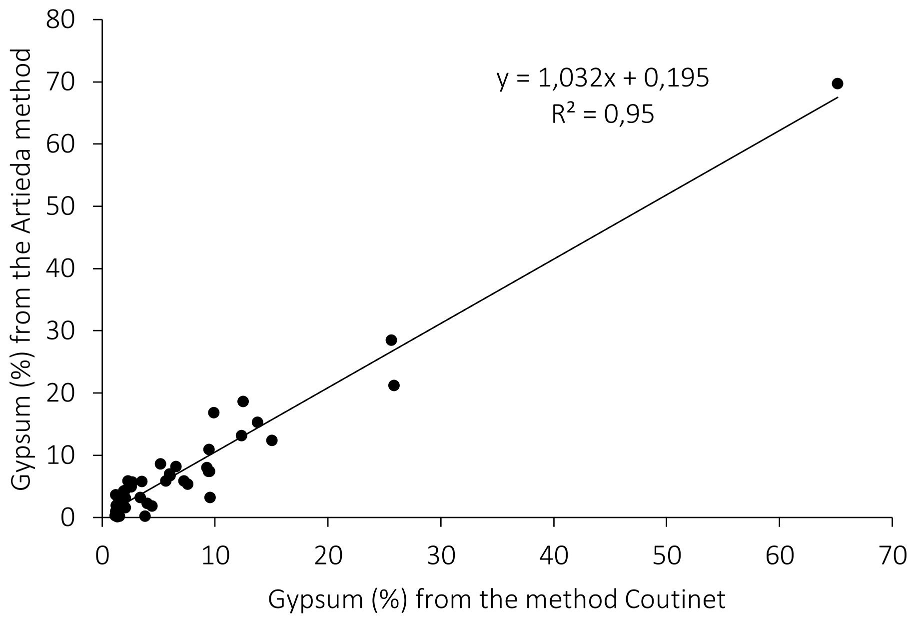


Figure 4. Gypsum content determined from the method Coutinet as related to gypsum content from the method Artieda

For the correlation between gypsum contents higher than 2 % (Figure 5), obtained by the two methods, the correlation coefficient is 0.94. Artieda et al. (2006), found a correlation coefficient of 0.98 for soil samples (Number of samples = 24) with contents between 2 and 50 %, by applying the two methods used in this article.

For samples with contents less than 2 %, the correlation is very weak (R^2=0.19). Artieda et al. (2006), found a correlation coefficient R^2=0.55. According to these authors, the method is not able to estimate the gypsum content of soils containing 2 % of gypsum accurately. According to Herrero et al. (2020), when the gypsum content is less than 2 %, the water released from the residual moisture in the sample affects the results, making a qualitative test of the gypsum necessary. For soils with a gypsum content < 2 % determined by the Artieda method, the gypsum content must be reported as < g % if the qualitative test for gypsum is positive, where g is the gypsum content obtained using this method (Artieda et al., 2006).

The use of this method is therefore encouraged, because the laboratory equipment used is very simple and it does not require the use of chemicals and it is easy to apply and quick. However, the chemical method of Coutinet (1965) takes a lot of time and requires the use of several chemicals which are expensive, harmful and dangerous for human health and the environment. Indeed, thermal methods for gypsum quantification in soils are easy and precise methods. They do not depend on the estimation of sulfates or calcium in the soil, leading thus to the absence of interference.

In the same context, According to Álvarez et al. (2022), gypsum can be fully quantified with relatively easy and inexpensive procedures, and the resulting quantification is accurate enough for a variety of uses. However, more sophisticated and costly techniques like acetone, turbidimetry, or thermogravimetry will need to be used when techniques capable of detecting extremely low amounts of gypsum (less than 2 %), are needed.

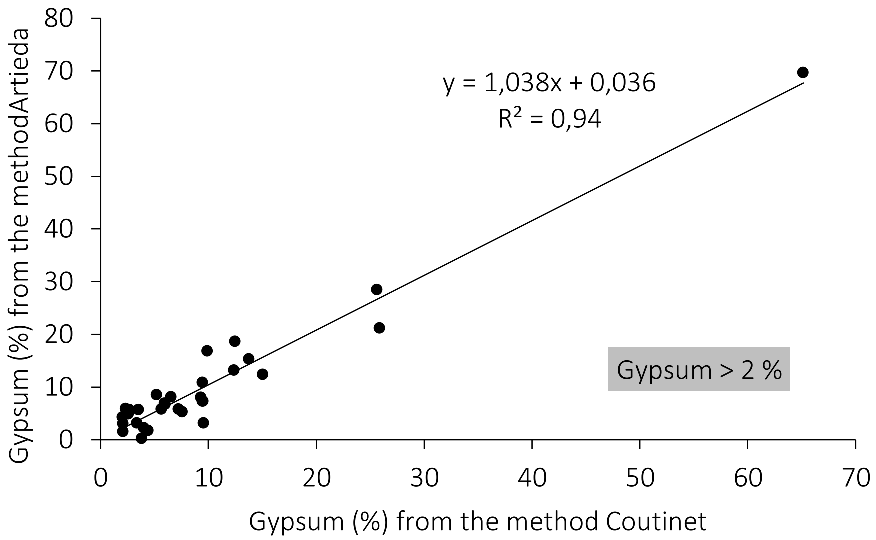


Figure 5. Gypsum content (> 2 %) determined from the Coutinet method as related to gypsum content from the Artieda method

4. Conclusion

The results of this work show that the samples studied, taken from soils presenting gypsum accumulations are in their majority slightly gypsiferous. We conclude that there is a high correlation between the two methods studied, namely the chemical method of Coutinet based on the precipitation of the sulfate ion with barium chloride and the Artieda method, measuring the weight difference that occurs when the sample is heated to specific temperatures and causes the loss of crystalline water from the gypsum molecule.

The Artieda et al. method is economic, fast and environmentally friendly because its application mainly requires only a precision balance and a ventilated oven. Summarily, the Artieda method offer formidable advantages over chemical method.

Author's declaration and contribution

The authors state that they have no conflicts of interest. YF contributed to conceptualization, methodology, investigation, writing of the original draft, and writing, reviewing, & editing of the manuscript. KD contributed to investigation, writing of the original draft and formal analysis. BF contributed to formal analysis, investigation and writing of the original draft. HAB contributed to supervision, methodology and conceptualization.

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