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A CLEANING METHOD BASED ON THE USE OF AGAR GELS: NEW TESTS AND PERSPECTIVES

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Abstract

For the peculiar artworks such as stucco plasterworks cleaning is troublesome for different reasons: weak mechanical behavior, high porosity and resulting water absorption, partial water solubility in the case of gypsum plaster. The choice of the cleaning method, especially as concerns gypsum based stucco materials, is crucial in assuring the lowest harmfulness possible together with a good level of efficacy. With the term agar we name a powder product composed mainly of polysaccharides and extracted from red algae species. When boiled with water, in a percentage range in between 0.5 and 5, it produces a colloidal solution that gellifies towards 35 °C. It can be used gelified and cold placed on a plan stucco surface, tepid and fluid poured on a surface relief or otherwise milled till a snow consistency, then pressed as a pad onto any surface; it has a high content of water which is slowly released into the porous substrate system. Hence the water-soluble components of soiling present on the surface are extracted and removed with the gel. Conservators should tune the following parameters to adjust the cleaning mode to a specific situation: agar powder concentration in water, application method (gel, tepid solution, "milled") and contact time. At the moment, agar gel is successfully used in cleaning gypsum plaster objects with grey coherent soiling deposits.

In our study agar was used in cleaning a dolostone capital. The power of agar in extraction of soluble salts was compared for different application methods and concentrations. The ions in the gel were analyzed with the aid of IC (Ionic Chromatography) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry).

Keywords: agar cleaning, salt extraction, ionic chromatography, ICP-AES

1. Introduction

Agar cleaning of artificial stone materials has been already applied on various artworks after its validation by several studies and lab surveys, in which its efficacy has been discussed and demonstrated (Anzani et al. 2008). At the moment, Agar gels have been successfully applied even on mural paintings, wooden ceilings and marble sculptures.

Agar Agar is a brand-name for a polysaccharide extracted form red algae of Gracilaria order composed mainly by Agarose and Agaropectine. Agarose is, due to its high molecular weight, responsible for the gel properties of Agar. The gel preparation starts by heating the mixture of the agar powder in water to 80-93 °C because of agar insolubility in water at room temperature. The fluid mixture (sol) is than allowed to cool

slowly and at around 30-40 °C it gels. The sol-gel process, in which agar passes from the random coil structure to organized three-dimensional network, is thermoreversible for several cycles. The melting and gel point temperatures may vary slightly due to the natural diversity in the Agar chemical composition influenced by the algae growing conditions and extraction/preparation technique. At room temperature the gel is quite rigid due its macro-reticulate structure based on the hydrogen bonds among the Agarose helices. This structure also allows to entrap enormous quantities of water either bonded to the polysaccharide molecules or free.

A general procedure for preparing agar starts by mixing 0.5/5 % in weight agar powder and de-mineralised water; then it is heated to 90 °C and cooled at room temperature. A solution of agar at 1.5 % is in the range 6.5/7.5 pH units. Agar gels have been used as aquagel cleaning systems with the ability to confine water action to outer surface of the substrate on which the gel is applied. Water is released in a controlled manner. The specific action and great advantage of agar gels, respect to traditional aqueous methods, dwells in its ability to entrap removed soiling into the gel structure itself.

It can be used in the fluid form, applying it while it is at a temperature in the range 40/50 °C directly on artwork surfaces; moreover it can be used in gel foils or "unstructured" after having it milled into a snow consistency, applying it with a spatula.

Agar gel allows to carry out cleaning operation on large or small areas, undercuts and surfaces not easy to reach, on vertical plan, moldings and ornaments. The formerly described performances are fruitfully used on gypsum plaster, since the slow and controlled release of water is especially useful when high water absorption capability, porosity and solubility features of gypsum are considered. Soiling is removed by agar gels by means of both a physical and chemical action. In fact agar gel, applied as a viscous fluid, forming an adherent thin film on a complete cooling, exhibit the ability to peel off soiling after its partial solubilization. The advantage consists in avoiding any mechanical stress of the treated surface taking into account that gypsum plasters are very sensitive to any kind of scrape, when wet. Still, the water release is limited even in case of agar in fluid and dense form (Figure 1).

Moreover, agar gels allow to calibrate the cleaning levels varying agar concentration, time of application and application technique (if fluid, milled or rigid gel). If the cleaning degree is not sufficient, the whole cleaning operation can be repeated. As to author experience no residues of organic substances are released onto the substrate (Anzani et al., 2008)

The conservator is helped in obtaining the desired cleaning level by agar gel transparency; in fact this feature allows a good control of the cleaning effect and at the same time the surface texture and morphology are magnified by a sort of "lens effect" which saturates the colors and puts in evidence micro details not visible at the naked eye.

The conservator should choose the correct gel concentration, the temperature of the gel, the time of application; preliminary tests should address the various parameters.

The viscosity of the solution is strongly dependent on temperature; gel is fluid for a longer time and consequently it can be applied at lower temperature, if it is prepared at lower concentrations. Agar gel is easy to remove and apparently no residues remain on the surface. On the contrary other types of gels demand a water wash after the removing. The rigid gels exhibit the lower adhesion force to the substrate, when compared to fluid

and milled ones. This point should be taken into account when a pulverised surface or a scarce coherent material is under conservation.

The "milled" or "unstructured" gel is useful in case of sensitive surfaces with a quite high level of relief, where the adherence and possible air bubbles at the interface could be a problem, giving a not homogeneous cleaning.

When the pure aquagel is not enough, a specific formulae could be tested containing surfactants, or polar solvents as ethanol or acetone. This choice could be successful when a hydrophobic material should be removed. Even chelating agents have been tested, for example on iron rust staining.

Currently is under test the use of agar gel as intermediary agent in laser cleaning. This innovative method combines a laser source (Nd:YAG λ=1064 nm and 532nm; Q-switch or Long Q-switch pulse regimes) with the agar gel. The laser radiation is addressed through the gel. As a consequence the laser energy is diminished. Advantages regarding a possible use on laser sensitive pigments such as lead white and cinnabar are under investigation. Moreover an increase in saturation is obtained when the artwork surface is wet with the agar gel, and this result is supposed to increase the substrate absorbing power and to limit the increase in surface temperature during laser ablation (Striova et al. 2012).

In order to test the effectiveness of the agar cleaning, the quantification of several ions (Na^+, K^+, NH_4^+, Mg^{++}, Ca^{++}, NO_2^-, NO_3^-, F^-, Cl^-, $C_2O_4^{--}$, SO_4^{--}) present in the aqueous solution extracted from stone materials by agar gels was performed by ion chromatography (IC) analysis, which in general detects and quantifies ionic species at µg/ml (ppm) level. The Mg^{++} and Ca^{++} concentrations present in solutions extracted from stone materials were confirmed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), which allows to quantify atoms and ions, mainly metals, down to ppb (µg/l) level with high precision and accuracy.

Fig. 1. Removing agar gel from a gypsum relief

2. Aims of the research

The present research aims at understanding variables that regulate the cleaning process of stone materials using agar gels. In particular, this study tries to determine the soluble salts extraction performances of agar gels applied with increasing concentrations and various methods. The cleaning ability is estimated by quantifying the soluble salts extracted from a natural stone substrate by agar gels. A point of interest is also the comparison of the concentration of extracted soluble salts with two different analytical methods: Ionic Chromatography (IC) and ICP-AES Analysis. ICP-AES is mainly used in the field of cultural heritage in geochemistry studies and in the characterization of metals artworks. As to author's knowledge, this is the first time that ICP-AES is used with the aim of detecting a concentration of metals in order to evaluate the effectiveness of a cleaning operation (Sansonetti et al. 2008).

3. Materials and Methods

In the present text the term "extraction" is used to indicate the uptake of soluble salts from the porous stone substrate by means of agar gels; while the term "recovery" refers to the quantitative removing of extracted salts from agar gels, giving a clear solution suitable for quantitative analyses.

3.1 Agar gels

With the term agar we name a powder product composed mainly of polysaccharides and extracted from red algae species of *Gelidium* and *Gracilariae*. Agar is composed of two polymer fractions: agarose and agaropectin. Agarose is a linear polymer (molecular weight 100.000 – 150.000) whose repeating unit is agarobiose, dimer -(1⟶3)-β-D-galactopyranose-(1⟶4)-3,6-anhydro-α-L-galactopyranose (Armisen, R. Galatas, F., 2000). Agarose is responsible for the gelling properties of agar. Agaropectin is a complex mixture of low-weight saccharide molecules and contains all the charges units, such as sulfate, pyruvate and carboxilate. Agaropectine has no gelling properties. The gel network of agarose contains double helices formed from left-handed threefold helices. These double helices are stabilized by the presence of water molecules bound inside the double helical cavity. The hydroxyl groups are arranged outside and allow for the aggregation of double helices into higher order assemblies termed *suprafibers* (Labropoulos et al, 2002). The agar powder can be dissolved in water at the boiling temperature, in a percentage ratio by mass in the range 0,5 - 5, to form a colloidal solution. This colloidal solution approximately gellifies at 35°C, forming a rigid thermoreversible gel that can be re-liquefied by heating it to about 80°C. Melting and re-gelification of the gel improves homogeneity and transparency. Gelified agar can be portioned by cutting, and applied on the surface to be cleaned in pads of appropriate form. It is also possible to apply the solution not yet gelified at the temperature of 50-60°C. Finally as already said, a further method of application is also to apply the gel slightly milled, which thus assumes a consistency similar to snow.

3.2 Angera stone capital

Cleaning tests with agar gels were performed on a fragment of a capital in Angera stone that belongs to the collection of the Civic Museum of Milan. The capital was kept in a warehouse at the Sforza's Castle in Milan, where a collection of stone elements coming from dismantled buildings of the town, is on display. The capital is affected by

surface decay phenomena such as pulverization and efflorescences, probably due to incorrect conservation conditions (Figure 2). Angera stone is a Triassic sedimentary rock, extracted in the southern part of lake Maggiore, chemically composed by a fine grain dolomite (total open porosity in the range 16-21%) (Alessandrini G., 1993). Agar gel, as already said, is an effective cleaning system on surfaces with the projection of figures or forms from a flat background, because of its ability in adhering perfectly to any detail of the profile; in this study a stonework was chosen as substrate for the tests because of its regular and plain external shape in order to better apply the agar pads in different areas, with comparable initial conditions (Figure 3). Moreover the aim of this study is to evaluate the capability of soluble salts extraction by agar, therefore a dolostone represents a good substrate because of the dolomite very low solubility in water at room temperature. Solubility product of dolomite, expressed in terms of activities, ranges from 10^{-17} to 10^{-20} (Jinghwa Hsu K., 1963); hence every ion detected during analyses should come from decay mechanisms. The pulverization phenomena which affect some part of the capital surface making it particularly fragile; so the agar gels cleaning method's advantages may emerge more clearly. A particular care was taken in selecting test areas that were chromatically as uniform as possible and that did non contain surface inhomogeneities. X ray diffraction analyses carried out on efflorescences sampled from the surface of the Angera dolostone capital, detected nitratine ($NaNO_3$) and gypsum ($CaSO_4$ $2H_2O$) as main components. Sampling in different points was carried out in order to check the homogeneity of soluble salts presence over the stone surfaces.

Fig. 2. The capital at the end of cleaning tests.

3.3 Cleaning tests

The first series of tests was designed in order to compare the extraction ability of gels prepared at equal concentration of 1% by mass, but applied in three different methods: fluid (colloidal solution at 50-60°C), gelified (rigid gel at room temperature) and milled (slightly whipped with a mixer). A second series of tests was based on the equal method of application (gelified pads) but four different concentrations were tested (1, 2, 3 and 4 w % of agar in water). Agar gels were prepared as follows: a weighted amount of powder was put into a suitable closed vessel filled with a known volume of water, then the vessel was heated using a microwave oven until the water began to boil. After cooling, the gel thus formed was heated again, then it was applied according to the three chosen methods. Agar was applied in test areas of 25 cm^2 (square 5x5 cm) in order to allow a comparable surface coverage (Figure 3). To obtain equal pad surfaces, fluid and milled agar was cast inside a suitable mold, once gelified it was cut with a blade at the correct size. With this method all the pads can be considered uniform in terms of cleaning area. Thickness was equal as well (1 cm). The contact time was the same for all the tests (3 hours). After this time lapse the pads were removed from the capital surface and they were sealed in a plastic envelope to be transported to the laboratory. A blank sample consisting of a 1% gelified pad, in size identical to those applied on the stone, but not used for salt extraction was also prepared and analysed as comparison.

Fig. 3. Capital of Angera Dolostone during cleaning tests with agar gels 1,2,3 % concentration in water.

3.4 Preparation of samples for ion analysis

After stone cleaning, the agar samples were divided in two equal parts (Figure 4); The first part was suspended in water for 24 hours on a vibrant platform; then the aqueous solutions containing ions recovered from agar was analyzed by IC (Na^+, K^+, NH_4^+, Mg^{++}, Ca^{++}, NO_2^-, NO_3^-, F^-, Cl^-, $C_2O_4^{--}$, SO_4^{--}) and ICP-AES (Mg^{++} and Ca^{++}). A

blank sample consisting of a 1% agar gel, in size identical to those applied on the stone, but not used for salt extraction was also prepared and analysed as comparison.

The second portion of agar gels were fragmented, filtered under vacuum, then suspended in a small volume of Milli-Q water (about 3 ml), filtered and thoroughly pressed on the filter, with the aim of recovering of the solution ions. The suspension in Milli-Q water and the subsequent filtration and pressing were repeated 5 times, in Milli Q water, in order that ion recovering from agar was quantitative as possible. Then the aqueous portions containing ions were collected and diluted to the final volume of 25 ml with Milli-Q water and analysed by means of ICP-AES.

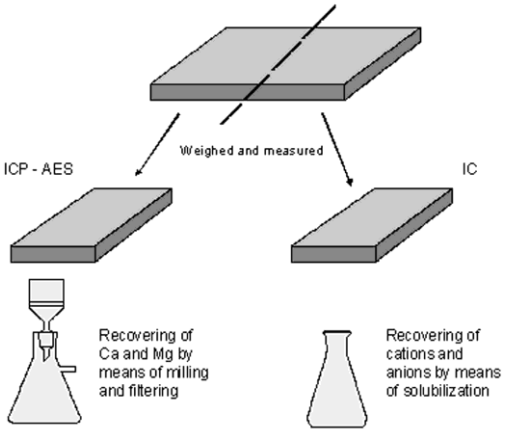

Fig. 4. Subdivision scheme of agar pad

3.5 IC analyses

Ionic chromatography analyses were carried out on the water solution extracted from the agar pads. Analyses were performed with a Dionex ICS-1000 ionic chromatograph. For the anions separation an AS19 4mm column with a ASRS ultra II self-regenerating suppressor has been used. The elution took place using a NaOH solution as eluent, with a concentration gradient from 10 to 60 mM and a flow rate of 0,25 ml/min. For the cations separation a CS12 4mm column with a CSRS ultra II self regenerating suppressor has been used. The isocratic elution took place using a 20 mM methanesulfunic acid solution as eluent with a flow rate of 0,25 ml/min. Injection was made with an autosampler and the injection volume was 25 µl. For quantitative analysis a specific multi elementary standard for both cations and anions has been used.

3.6 ICP-AES analyses

Magnesium and calcium concentrations of aqueous solutions extracted from stone materials and recovered from agar samples were determined by ICP-AES analysis.

Table 1 provides information on the apparatus and experimental conditions for the determination of Mg^{++} and Ca^{++}.

Table 1. ICP-AES apparatus specifications and analytical conditions for the determination of Mg^{++} and Ca^{++}.

Spectrometer	Instruments SA, Jobin-Yvon 38 Sequential (France)
Monochromator	Czerny-Turner mounting
Nebulizer	Meinhard pneumatic
RF power	1.0 kW
Argon flow	auxiliary flow:14 l/min
	sheath flow: 0.15 l/min
	aerosol flow: 0.35 l/min
Nitrogen flow	1 l/min
Sample feed	1.2 ml/min
Analyte line [Mg]	280.270 nm
Analyte line [Ca]	393.366 nm
Reference line [C]	193.091 nm

Calibration was performed using Mg and Ca standard solutions (Aldrich Chemical Co., Milwaukee, WI, USA) in Milli-Q water.

4. Results

4.1 IC results

Comparing the results obtained for the agar gels at 1% (percentage by mass) applied with different methods, allows some fruitful considerations (Figure 5). In particular the sulphate content (as regards anions results) and calcium (as regards cations results) are considered the most significant. These two ions are deemed as particularly meaningful because they are connected to the sulphation phenomena that affects carbonatic materials such as Angera stone. The obtained results on sulphate and on calcium content suggest that both the milled and the fluid gels have a higher extraction force compared to the gelified application method (Fig. 5). Low values of ions detected in the blank confirmed the absence of soluble species in the agar raw powder used for the preparation of gels. Other ions, in particular nitrates, show trends more difficult to interpret. This can be explained by considering that these ions are usually connected to very soluble salts that can migrate and concentrate locally within a inhomogeneous substrate such as the Angera stone.

The second series of tests concerns gelified pads with increasing concentration of agar powder in water. In this case the cations concentration trend suggests that agar extraction power improves with increasing concentration. This consideration is valid also in the case of chlorides and sulphates; on the contrary, nitrites and nitrates show very high values locally due to the aforementioned high solubility of the salts to which they are possibly associated.

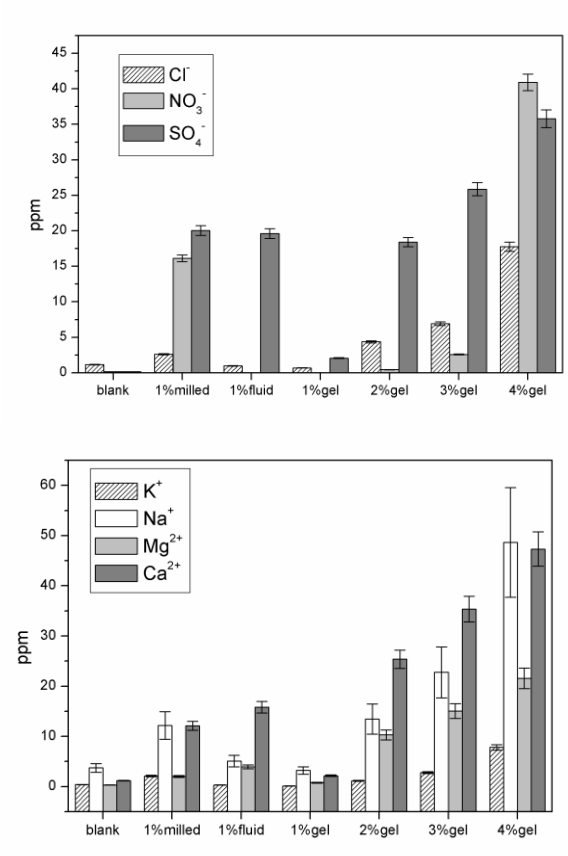

Fig. 5. Concentrations of anions and cations detected with IC analysis.

4.2 ICP-AES analysis

Figure 6 shows the magnesium and calcium concentrations of aqueous solutions extracted from stone materials and recovered from agar pads prepared with different concentrations of agar (1-4 %) and in different modes (gelified, milled and fluid).

ICP-AES data for Mg^{++} and Ca^{++} confirm those already observed by IC, since they show that the gelified agar sample at 1 % contains the smallest concentration of both the metals, while milled and fluid samples containing agar at 1 % display the highest concentrations of both ions. These results suggest that milled and fluid agar are able to extract higher amounts of ions from stone with respect to the gelled agar, By increasing the agar concentration in the gelled agar, the concentrations of both ions increase almost linearly, suggesting that the higher the agar concentration, the higher level of extracted ions.

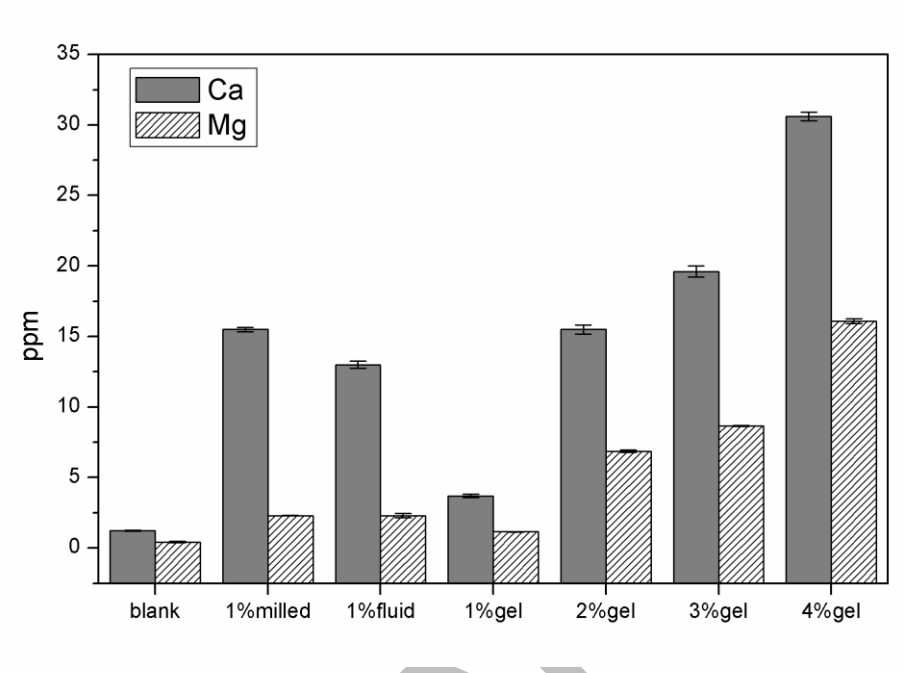

Fig. 6. Concentrations (μg/ml) of Mg^{++} and Ca^{++} in aqueous solutions extracted from stone materials and recovered from agar samples prepared with different concentrations of agar (1-4 %) and in different modes (gelified, milled and fluid). Blank sample was used as comparison (see text).

5. Conclusions and perspectives

The survey focused on the attempt to compare the soluble salts extraction ability of various agar gels applied at different concentration and with various methods. This kind of survey is very troublesome in real cases because of salt distribution inside the stone substrate, that we are not able to evaluate precisely as regards its homogeneity. Anyway the checks by means of XRD on powders sampled from different areas, gave very similar diffraction patterns.

As regards the various application systems, the better ability in extracting ions by means of milled and fluid agar is probably due to a higher water release onto the surface, an higher specific surface area and because they can better adhere to the stone surface compared to the gelified agar pads.

As regards the agar gels with increasing concentration, the ability of salt extraction is proportional to the gel concentration. A possible chemical role of the polysaccharides has to be taken into account in attempting to explain these data.

IC and ICP data display a comparable trend as concerns calcium and magnesium (Figure 7); a significant aspect of this study was to verify the IC reliability in studying salts concentration coming from a stone substrate, compared with another analytical technique.

Work is in progress in order to understand the transport phenomena of water release at the interface agar/stone substrate.

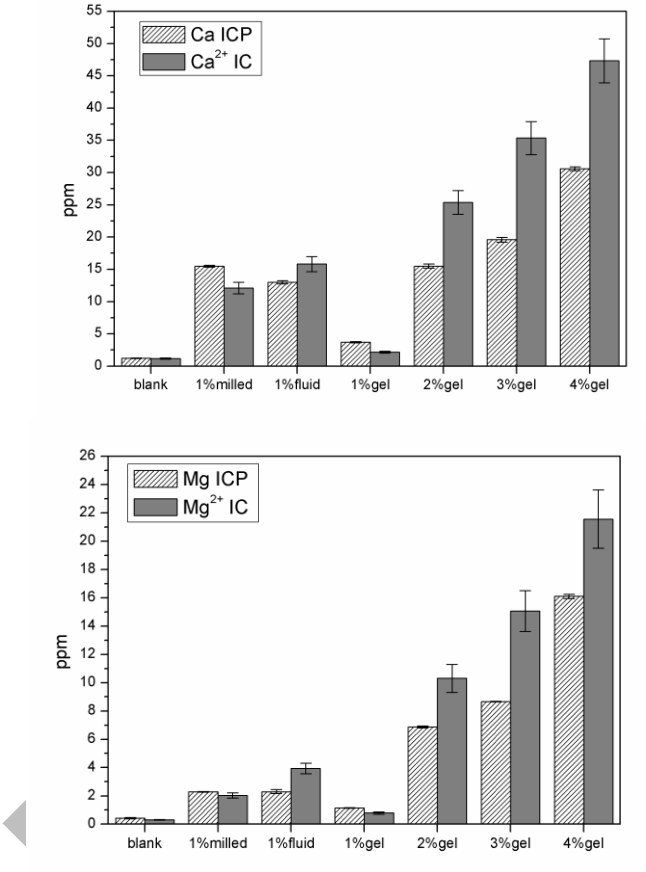

Fig. 7. Comparison between results of calcium and magnesium detected by means of IC and ICP-AES.

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