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REVIEW ARTICLE

Misused terms in analytical chemistry with emphasis on ultrasound application

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A wide number of analytical terms have been applied erroneously for many years by analytical chemists, and they apply at present yet, by considering the time makes their use correct. The question is, may precedents validate the present use of incorrect scientific terms? Misused terms are found along the analytical process, starting with giving the name of the sample to the exiguous fraction of the original sample that reaches the detector or the high-resolution equipment after sample pretreatment and sample preparation. All the steps of the analytical process are considered in this article, with special emphasis on sample preparation and, within this, on the use of ultrasound, mainly for assisting extraction more unequivocally named as leaching or lixiviation. A call of attention in this respect is considered by the author to be of help to the analytical community.

KEYWORDS
sample preparation, sample pretreatment, ultrasound-assisted extraction

1 | MISUSED TERMS IN THE ANALYTICAL PROCESS

Before centering the subject of this reflection on the analytical use of ultrasonic energy, some general analytical misuses require to be considered because they are widely applied with impunity in scientific journals in general, but with a higher charge of guilt when they appear in analytical journals.

There is a number of analytical terms applied erroneously for many years by analytical chemists, and they apply at present. They consider the time makes their use correct. The question is, may precedents validate the present use of incorrect scientific terms?

By taking a walk along the analytical process, some considerations could contribute to thinking a bit about the correctness of the words before writing them.

It is well known by analytical chemists that the steps mediated between sampling and the solution ready to be inserted either in the detector or in high-resolution separation equipment that precedes the detector have been collectively known as sample preparation. Nevertheless, it is clear that some steps, particularly the first steps after sampling, are mainly mechanical, physical steps, applied without altering the composition of the original sample, except in water content. As can be seen in Figure 1, these steps can consist mainly of grinding, sieving, drying, or lyophilization, even partial water removal, in the case of liquid samples. May, one or several of these steps be comparable to leaching, by which most of the solid sample components remain as such, providing an appropriate leacher is used? Perhaps can they be similar to liquid–solid extraction, in which a suitable sorbent can retain practically only either

Article Related Abbreviations: SP, sample preparation; UAE, ultrasound-assisted extraction; US, ultrasound

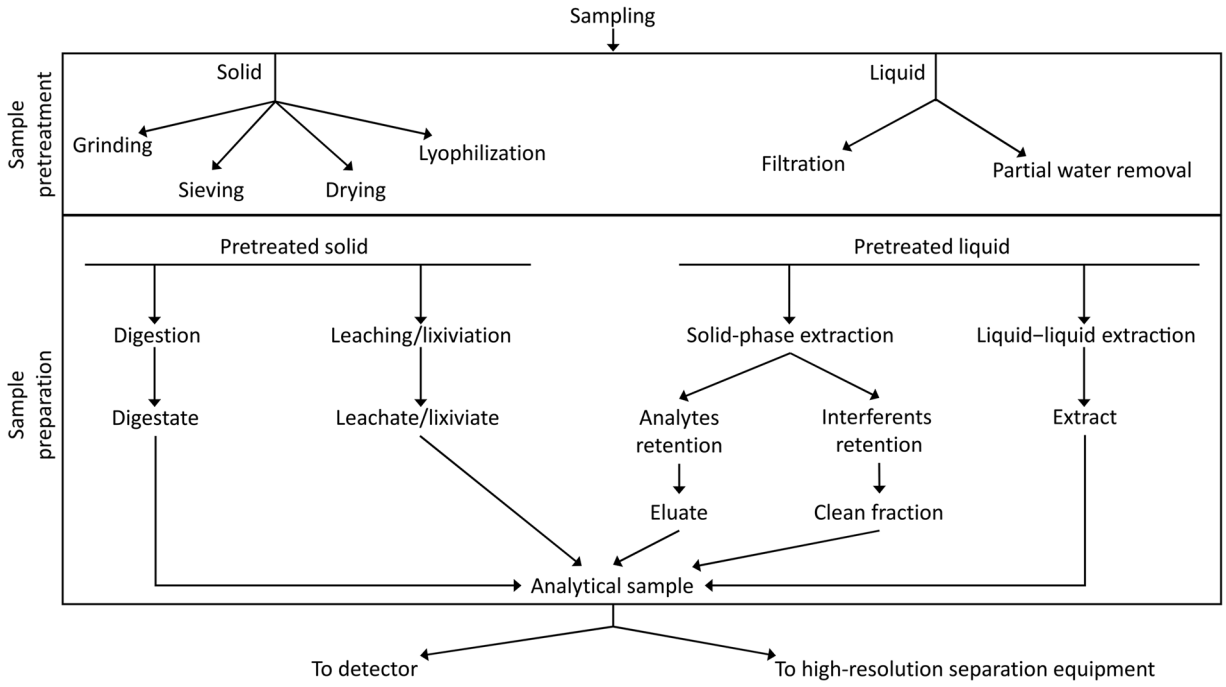

FIGURE 1 Steps of the analytical process and name(s) of each

the target analyte(s) or a major part of potential interferents? Similarly happens in the case of liquid–liquid extraction, in which a suitable extractant can accept in a selective way the desirable components from the donor phase.

On the other hand, should extraction steps of different nature be expressed only by "extraction" without adding another term that clearly establishes the type of phases involved? Usually solid–liquid extraction is known as extraction, but should it be more correct to be named as leaching or lixiviation, which clearly expresses the involvement of a solid and a liquid that more or less selectively separated components from the solid? Should this more or less selective liquid be named as leachant, lixiviant or is it better to use the generic name of extractant or even liquid phase? Should the liquid resulting from the leaching step be named leachate, lixiviate or a more generic and confusing name of extract should be more appropriate?

Differentiation between the former steps and those that clearly alter the composition of the original sample should be established. The names of sample pretreatment and sample preparation (SP) should be the most appropriate for the former and latter, respectively.

Despite sample pretreatment could be considered a non-influential step, its nature can be crucial in the subsequent behavior of the target analytes. This is the case in the comparison of fresh, lyophilized, and oven-dried orange-peel samples, in which the content in aglycons increased to the detriment of their glycosides from fresh to lyophilized to oven-dried orange-peel samples [1]. Also, significant differences in the concentration of 44 out 74 metabolites in *citrus limon* samples of fresh material as compared to those subjected to either oven-drying or lyophilization have been found [2]. Therefore, sample pretreatment could sometimes be a crucial step.

A common error in dealing with the names of the fraction obtained after any sample treatment is to keep the name of "sample" along the steps to reach the detector or the high-resolution equipment, even when a minimum fraction of the original sample is present, providing the applied treatment is enough selective. From Figure 1 it is clear that the name of leachate or lixiviate is the most appropriate for the liquid phase resulting from this step, as the name of the extract is confusing in this case. Similarly, the eluate is the fraction obtained when the proper liquid (eluant) has been circulated through the sorbent in which the target analytes are retained and removed from the solid phase. In the less common case in which the sorbent is used for retaining interferents, the non-retained liquid that circulates through the sorbent should receive the name of "clean fraction" from the previous step (e.g., if the liquid subjected to solid-phase extraction had resulted from a leaching step the name would be "clean fraction from the leachate"). Finally, the extract is the name given to the immiscible phase after transference of the target components from the donor phase in a liquid–liquid extraction. Maybe an adjective should be added to extract to ratify it comes from liquid–liquid extraction and not from solid–liquid extraction.

Any of the solutions ready for being inserted in the detector or in high-resolution equipment is an "analyt-

ical sample". This generic name is shortened by most researchers, who use the word "sample" to name any solution from any step after which each time the less representative part of the original sample is contained. A great deal of misunderstanding in this context could be avoided by using the correct, unequivocal name of the solution that results after each specific treatment [3].

In dealing with the last steps of the analytical process, the detection, determination, or measurement of target analytes is frequently attributed to a separation technique such as chromatography (e.g., determination of given compound(s) by LC or GC). Despite it is clear for analytical chemists that chromatography only separates, the fact that the separation column is inexorably coupled to a detector, makes this to be considered as a part of the chromatograph. This is particularly true in the case of very common detectors such as molecular absorption detectors or flame ionization detectors connected to liquid or gas chromatographs, respectively, but not in dealing with mass detectors. Is not the chromatograph performing the same task independently of the subsequent detection step?

On the other hand, clear differentiation between technique and method should be a matter so far overcome by scientists in general and analytical chemists in particular. It seems incredible that presently we find in analytical journals sentences such as "The Soxhlet method is a well-established technique [4]", or "The ultrasound technique is a safer, more economical and greener method … [4]". By looking at Wikipedia, the following is found as the definition of analytical technique "Analytical technique is a method that is used to determine a chemical or physical property of a chemical substance, chemical element, or mixture", thus clearly contributing to increase confusion. While a technique is a scientific principle that can be materialized in a given instrument, a method results from the application of the instrument under given, optimized conditions to a target sample in which some compounds require to be studied.

Just to criticize some very common and useless words very applied in SP is as follows: "This variable (e.g., temperature) was studied at three different values", is it necessary to establish that the values were different or without this adjective the values could be all three the same?

2 | ERRONEOUS WORDS USED IN GENERAL ANALYTICAL ASPECTS OF ULTRASOUND

Ultrasound (US) is a type of non-radiant energy — therefore, it is incorrect to express its application as "US irradiation", which continues being used presently (e.g. at different levels of ultrasonic irradiation [5])— each time more used by analytical chemists. Nevertheless, the knowledge on the fundamentals of US has not grown at the same rhythm as its use. In fact, cavitation, the most popular phenomenon caused by the high-power US, is explained in the introduction of most of the articles in which this energy has been used by using a copy-paste of books on US [6].

The main effects of the cavitation phenomenon are the thermal effect (very high temperatures occurring at the microzone level), mechanical forces, and shear forces (created by microstreaming and shock), and free radicals generated by ultrasonolysis in either water or other polar liquids. All these effects are highly dependent on the US frequency, property scantly considered by some of its users; even sometimes it is forgotten when US equipment is described.

As the name implies, the frequency of US is beyond the sound frequency. Nevertheless, the prefix "sono" and the adjective "acoustic" are used in dealing with US (e.g., sonochemistry is a term used in US application on chemistry). This error should be avoided as the US range encompasses from 20 kHz (human hearing reaches up to 16–18 kHz) to GHz, with the division between high-power US (20–100 kHz) within which cavitation is a predominant force, and diagnostic US (5 MHz–GHz) [7]. A "sonochemistry range" is considered to encompass from 20 kHz to 2 MHz, in which the zone within or close to MHz is considered therapeutic.

In general, the use of sonication is more frequent than ultrasonication, even a mixture of both can be found as in the case "40°C extraction temperature, 50 W ultrasonic power, and 40 min sonication time [8]". Also "sonicated by ultrasound", "UAE uses acoustic waves" or "a volumetric flask is placed in an ultrasonic bath, then sonicated" are frequent at present in articles on UAE [9]. Also, the name of an Elsevier journal seems to be contradictory: Ultrasonics Sonochemistry.

3 | CORRECTIONS RELATED TO US DEVICES

The two most common US devices used in analytical chemistry are ultrasonic cleaning baths and ultrasonic probes.

Most analytical chemists who start to work with the US for SP use an ultrasonic cleaning bath. This device (omnipresent in almost any laboratory) is designed mainly for cleaning glassware and degassing, and in it, ultrasonication is not uniform, and the power into the target system declines over time. This irreproducibility source

affects the results of the analytical method in which the step is involved. In addition, not all US cleaning baths operate at the same frequency–a fact that can significantly affect the results, and constitute a serious shortcoming in dealing with reproduction of a reported method.

US probes are also known as horns or sonotrodes. In addition to being not subject to the irreproducibility problems of ultrasonic cleaning baths, probes are endowed with the versatility of power and duty cycle programming as required.

The better performance of probes as compared with cleaning baths leads to inappropriate attributions inadmissible for analytical chemists. For example, the name of "instrument" given by some authors to US probes [10] must be avoided as these devices never provide analytical information.

Some authors attribute to probes a "focused" action, which can even appear in the title of the article [11]. Users must be aware that there is not a guide for US in the probe, as is the case with waveguides in some microwave devices [12].

Also, the discontinuous application of US, correctly expressed as duty cycle, deserves to be clarified. The correct way to express this parameter is as the number of times units of application per total units of the cycle (e.g., 5 s/9 s) or as a fraction of the unit of time that US application lasts (e.g., 0.5 s/s). To express this parameter as a percent is incorrect as, in this way, no information is given about how long each US application lasts.

A non-fortunate attribution of US is the generation of pulses [9]. Despite US can be applied in a continuous or discontinuous way, no pulses can be provided by a US generator in a way similar to laser devices.

The nil or limited importance US users give to the device for application of this energy is shown by the also nil or scan information they provide about its characteristics, most times. This information ranges from no information at all [13], information about the model of the device [14], that about US power and/or intensity applied [15] or about frequency [16], to enough information about all characteristics that made possible to reproduce a given experiment. In providing enough information, a distinction should be made between devices providing single or multiple frequencies of US. In the former case, the most common information is frequency, and either, power or intensity for probes [17] or baths [18]. Especial care should be devoted to variable units, without confusion between US power (W), and US intensity (W/surface unit, usually cm^2) [19]. Always, detailed values of the US variables should be included in publications, at least as Supporting Information.

4 | US IN SAMPLE PRETREATMENT

Despite US has been used in analytical chemistry mainly for SP, also preliminary steps (sample pretreatment) have been improved by the application of this type of energy. Examples of improvement in freezing or in crystallization appear in the literature [20]. Lyophilization processes have also taken advantage of US applications that supplied additional sublimation energy without sample heating —avoided by discontinuous US applications with short duty cycles [21]. US also breaks the cell integrity of vegetal cells thus favoring pectin de-esterification [22]. Nevertheless, US is not always the panacea, as this type of energy also causes undesirable effects, mainly owing to degradation [23]. In these cases, the use of higher US frequencies is recommended to decrease cavitation, the main reason for these effects.

5 | ANALYTICAL MISINTERPRETATION ON THE EFFECT OF US TO ASSIST EXTRACTION

Leaching or lixiviation has been the analytical step more widely assisted by US, but never under one of these two names, US-assisted extraction (UAE) and USAE, that have been the names given to the technique or to the methods based on it, among which UAE is used below.

The fact that US application does not increase the temperature of the system is one of the reasons why this energy is considered as a suitable option to extract thermally unstable metabolites present in a solid sample (also in biological fluids, cells, or organisms) under a given set of physiological conditions. Nevertheless, the lower operating temperature in UAE, as compared to microwave-assisted extraction, for example, does not avoid the degradation effect of free radicals formed by polar extractants. The degradation effect is shown as a decrease of the extraction yield by increasing the extraction time when the process is monitored by an unselective detector (viz., a detector based on molecular absorption) [24]. This old error is also committed at present [5]. Therefore, appropriate analytical equipment (e.g., a chromatograph coupled to a suitable mass detector) could provide information on the very probable degradation of the target compounds and the type of products formed in the process. This is especially important in dealing with extracts to be used in food production, owing to the potential toxicity of the degradation products.

Similarly, a comparison between UAE and Soxhlet extraction should not state that the former is less degradant because the overall temperature reached in the system is lower than that reached in Soxhlet extraction. The authors

working with the high-power US must know the principles of US, and thus, the very high-temperature microzones reached in a US-assisted system, which can alter the system components even more than several hours of Soxhlet extraction.

It is very enthusiastic to consider UAE as "green" in a given method because it requires less extractant than its counterpart Soxhlet method or because "it is more energy-efficient than Soxhlet" [2]. How the calculation of the energy has been made in each case? What is the amount of a given extractant to consider a method as green independently of its chemical characteristics?

6 | ASPECTS TO BE TAKEN INTO ACCOUNT IN DEVELOPING A UAE

When planning an exhaustive study of US parameters the researchers should take into account the importance of the parameters to give them the appropriate priority. For example, to take into account the liquid/solid ratio, US power, temperature and extraction time, and event solubility of the target compounds should be extracted in the selected extractant, but without forgetting the value of US frequency [25]).

The present trend of promoting green extractants has led to the use of oils in UAE. However, oils as extractants have a limited application as they can only be used to be enriched with the components from the solid that can be transferred to the lipids. Isolation of the transferred compounds is a very difficult task. In addition, it is of paramount importance to know that US drastically affects oil stability. This behavior was clear in a study on oils' stability in which stable extra-virgin olive oil showed severe rancidity after a few hours of US application [26].

Special conditions should be adopted when volatile components are extracted with the help of US, as it is well known that US application favors removal of volatiles from solids and liquids (a common example of this behavior is the use of US cleaning baths for degasification of chromatographic mobile phases). Examples of erroneous uses are the UAE of volatile components from saffron in an open atmosphere without protection for losses of both the target compounds, after transference to the liquid extractant, and the volatile nature of it (ethanol–ethyl acetate mixture) [27, 28].

The difference between technique and method is not clear at present for some authors who develop methods based on UAE: "UAE has advantages of simplicity, and is less time consuming and uses less solvent than other methods, and can be easily coupled with other extraction techniques" [9]. In fact, it would be very complicated to couple a method to a technique.

7 | CONCLUSIONS

Adoption of the appropriate word, particularly in science, is of paramount importance. Applying an inappropriate term based on its frequent use should not be allowed.

To teach in research involves not only training in the laboratory but also strict control of how the researcher expresses the results he/she obtains. Both editors and reviewers have a hard task in this area.

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CONFLICT OF INTEREST

The author has declared no conflict of interest.

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