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Quantitative phase analysis of hydraulic limes using the Rietveld method

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Abstract

Quantitative phase analyses of three commercial samples of hydraulic limes have been performed using the Rietveld method. Although the Rietveld method has been already applied to cement analysis, we report here the first application to different classes of hydraulic binders, such as hydraulic limes (HL) and natural hydraulic limes (NHL). Unlike HL, that are simple diluted cement, NHL are specific product of great interest for its application in building restoration and conservation.

Samples were also characterized by laser granulometry and chemical analysis. Thermogravimetric analysis/Differential Scanning Calorimetry (TG/DSC) and calcimetric analyses were conducted to compare the results of such well-established techniques with those obtained with the Rietveld method. Taking advantage of the Rietveld method with the addition of an internal standard, the phase fraction of all the crystalline phases as well as the amorphous component, have been accurately determined. This technique offers a valid support for the characterization of hydraulic limes in the light of the EN classification of such industrial products.

Keywords: Calcium-silicate-hydrate (C-S-H); X-ray diffraction; Thermal analysis; Amorphous material; Carbonation; Rietveld method

1. Introduction

The discovery, during the eighteenth century, of the hydraulic properties of a mixture of limestone and clays burned at about 1200 °C, made the hydraulic limes the historical precursors of portland cement. With respect to air limes, also known as fat limes/putty limes/hydrated limes and calcic limes, hydraulic limes harden because of their tendency to react with water. A systematic classification based on the ability of such materials to set under water was introduced by Vicat and published in the nineteenth century [1]. These hydraulic binders were progressively abandoned with the advent of portland cement, which provided quicker set and greater strength. Nevertheless, recently there has been a renewed interest in hydraulic limes, because of their use in the conservation of historical buildings, where direct and indirect damages caused by the introduction of cement mortars, gauged or not with air limes, have been extensively documented [2]. Cement is too hard, rigid and impermeable; furthermore, it contains more soluble salts, which may develop surface defects and high crystallization pressures that can be very harmful for building conservation. Moreover, cement is characterized by a completely different pore size distribution from original stone and mortars. This property determines the water movement, moisture escape and salt crystallization in masonry.

Nowadays, hydraulic limes can differ significantly from those of the early days. The EN459-1 normative [3] describes two distinct categories:

1. *Natural hydraulic limes (NHL)*: limes produced by burning more or less argillaceous or siliceous limestones, with subsequent slaking, with or without final grinding.
    1.1 *Natural hydraulic limes with additional material (Z)*: special products that may contain added suitable pozzolanic or hydraulic materials up to 20 wt.%.

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2. *Hydraulic limes (HL)*: limes mainly consisting of calcium hydroxide, calcium silicates and calcium aluminates produced by a mix of suitable materials.

Actually, HL are a dilute form of hydraulic binders like pozzolana or cement, whereas NHL are produced directly from a single raw material, at a burning temperature of around 1200 °C. The burning temperature, well below that of portland cement, leads to a different mineral association [4]. During burning, the decomposition products of clays and lime react to form silicates and aluminates. The final result is a mixture of cement phases, inert material (like silica and other minor silicates) plus unreacted lime and clays. With regards to phase equilibria, under 1250 °C, dicalcium silicate (C_2S) should be the dominant silicate. C_2S will be in part converted to tricalcium silicate (C_3S), with the addition of CaO, only at higher temperatures. However, C_3S can be found in NHL due to the presence of 'hot spots' in the kiln. On the other hand, residual inert materials may still survive as a result of incomplete burning. The aluminates are mainly tricalcium aluminate (C_3A) and gehlenite (C_2AS). Unlike C_3A, gehlenite is not found in normal portland cements, although it occurs in some calcium aluminate cements. After burning, the lime needs to be slaked with enough water to convert it to calcium hydroxide. This step is crucial for the quality of the final product, since the content in free lime should be as low as possible, and, at the same time, reaction of water with silicates and aluminates must be avoided to preserve hydraulic properties.

Hydraulic and natural limes have the property of setting and hardening in water. Furthermore, atmospheric carbon dioxide, which transforms portlandite into calcite, and hydration of several hydraulic compounds which form hydrated calcium silicates contribute to the hardening process.

Since setting and hydraulic properties of cementitious materials are strictly dependent upon phase composition and structure of crystalline phases, quantitative assessments are crucial to assure quality control. Several methods have been tested so far, most of them being very time consuming, like microscope point counting or selective dissolution. X-ray powder diffraction (XRPD) was recognised as one of the most promising technique for cement characterization. However, in the past, phase fractions were calculated by conventional powder diffraction method using the relative intensity of the major peaks of each phase in the sample. Due to the superimposition of peaks of many aluminate and silicate phases, this is a very challenging task for cementitious materials, often leading to unreliable results [5]. The Rietveld method, originally conceived for crystal structure refinement, overcomes these problems with a completely different approach. It allows for the weight fraction of each phase in an unknown mixture to be calculated using the entire powder diffraction profile, and not only the integrated areas of few peaks. The refinement is a fitting procedure in which the difference between the experimental powder diffraction pattern and the calculated one, together with a background function, is minimised. This method requires the knowledge of the crystal structure of all the phases present in the sample. The typical sources of error in conventional X-ray diffraction analysis, such as preferred orientation, solid solutions or peak overlapping, can be minimised or taken into account by introducing corrections with rigorous physical meaning.

The weight fraction W_α of each phase α in the sample, is defined as [Eq. (1)]:

$$W_\alpha = \frac{(2S_\alpha \rho_\alpha \mu_m V_\alpha)}{\rho_m}, \tag{1}$$

where S_α is the scale factor of phase α calculated by the refinement program, ρ_α is the density of phase α, μ_m is the mean absorption coefficient of the mixture, V_α is the volume of the phase α, and ρ_m is the density of the mixture. Since during the calculations it is assumed that the sum of all the weight fractions is equal to 1 (normalization condition), Eq. (1) is valid if all the phases present in the sample are included in the refinement. If an amorphous component is present, the normalization condition does no longer hold. In this case, the correct weight fraction for each phase can be calculated by spiking the sample with a known amount of an internal standard. The values obtained from the refinement should thus be rescaled considering that the weight fraction of the standard obtained from the refinement ($W_{\mathrm{Std\ Rietveld}}$) will be higher than the real one (W_{Std}). In general, we can write:

$$W_\alpha = \frac{(W_{\alpha\ \mathrm{Rietveld}} W_{\mathrm{Std}})}{W_{\mathrm{Std\ Rietveld}}} \tag{2}$$

Thus, the error in the estimation of phase α depends basically on the errors in the refined scale factors S_α and S_{std}. To minimise these errors the internal standard should be well crystallized and chosen in order to reduce peak superimposition with the diffraction pattern of the sample. A critical point is the choice of the amount of internal standard to be added to the mixture [6,7]. The percentage of the amorphous component (W_A) can be calculated directly from the estimated weight of the internal standard according to the equation (Eq. (3)):

$$W_A = \frac{100}{(100 - W_{\mathrm{Std}})}\left[1 - \frac{W_{\mathrm{Std}}}{W_{\mathrm{Std\ Rietveld}}}\right]. \tag{3}$$

As for all analytical methods, attention should be paid in sample preparation, even if this procedure should not take more than few minutes. Time for data collection instead can range widely, due to the instrumental set-up. With conventional equipment, this step is by far the most time consuming. Times of several hours for data collection, and the need for personnel with specific scientific background, have been for years the main factors limiting the diffusion of XRPD with the Rietveld method in the industrial world.

Table 1
Samples used in this study

Sample	Type	Classification (following EN459)	Colour
1	Hydraulic lime	HL5	Light brown
2	Natural hydraulic lime	NHL 3.5	Grey
3	Natural hydraulic lime	NHL 3.5	White

The situation has substantially changed in the last years, thanks to the great efforts made mainly by instrument manufacturers; nowadays, very fast detectors are commercially available and are capable to drastically shorten the time for data collection without loss of resolution [8]. Moreover, the Rietveld codes have been re-implemented and are now more user-friendly (see for example the new graphic interface of GSAS, EXPGUI [9]).

2. Experimental procedure

This study deals with the characterization of three different industrial products, namely natural hydraulic lime, classified by EN 459 as NHL 3.5, and hydraulic lime classified as HL 5 (see Table 1). As reported in the literature [4], hydraulic limes undergo rapid deterioration by air exposure. Three reactions are involved: the hydration of free lime to form portlandite [$Ca(OH)_2$] thanks to air humidity; the carbonation of portlandite that, reacting with atmospheric CO_2, forms calcium carbonate; and the hydration of hydraulic phases (CS and CA). Thus, the amount of CaO, $Ca(OH)_2$, and $CaCO_3$ is changing in time when the sample is exposed to air. The net result is the total consumption of free lime and a substantial increase in the content of calcium carbonate. Thus, in order to correctly compare the results of different analytical techniques, analyses should be conducted on absolutely identical samples. To do so, each sample was kept sealed until use, and X-ray, TG/DSC and calcimetric measurements were accomplished simultaneously. However, since phase composition could change when the sample is under measurement, a correct choice of total time for data collection was necessary. To this aim, a preliminary investigation was conducted exposing a sample of hydraulic lime to the air (at room temperature and relative humidity of 50% for 1 week). At fixed time intervals, a small amount was taken for carbonate determination by calcimetric method. On the basis of these results, adequate XRPD data collection parameters were chosen.

Powder spectra were collected at ambient conditions with Cu K_α radiation, in the range 5–80 $^\circ 2\theta$, using a laboratory Philips PW1729 Bragg–Brentano diffractometer equipped with a gas proportional detector. Counting time was 5 s for each 0.02 $^\circ 2\theta$ step. Corundum NIST 676 was added to the mixtures (10 wt.%) and used as internal standard. As described in the Introduction, this combined Rietveld and RIR (Reference Intensity Ratio) method allows the estimation of the amorphous phase. The cell parameters were refined together with the coefficients of the function modelling the background (a six-term cosine Fourier series) and of the pseudo-Voigt function modelling the profile function of the Bragg peaks. Refinements were conducted by the Rietveld method using the GSAS [10] and EXPGUI [9] packages. Preferred orientation for some crystalline phase was taken into account using the March–Dollase algorithm. Structural models for all the phases were taken from the ICSD database [11]. GSAS allows for a maximum of 9 phases to be refined simultaneously (in our case 8 plus the internal standard). This number is usually enough for most polyphasic systems, however, in our case, two samples revealed the presence of 9 phases and hence, the least abundant phase was necessarily discarded. Obviously, this implies essentially an error in the estimation of the amorphous phase. For both samples, the weight fraction of C_3A (about 1%) was not reported in the corresponding table, although indicated as present. Chemical analyses by X-ray fluorescence were conducted with a Philips PW1480 spectrometer. SO_3 content was determined by gravimetric method. CO_2 was determined by gas volumetric method (calcimetry), reporting the mean over three measurements.

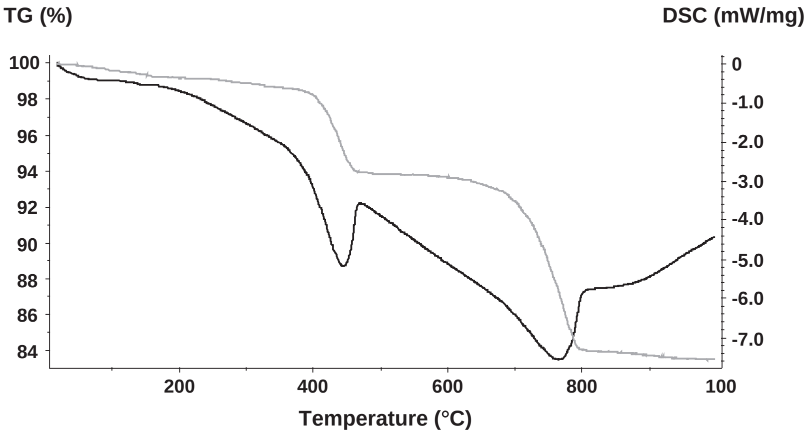

Fig. 1. Thermal analysis curves (TG/DSC) for sample 1. TG curve in grey. Calcite was clearly identified as responsible of the weight loss at about 800 °C.

Table 2
Particle size distribution as cumulative volume fraction

Particles diameter (μm)	1 (%)	2 (%)	3 (%)
8	31.0	28.3	32.4
16	42.1	40.6	42.0
32	61.3	60.6	63.6
63	85.0	81.8	88.6
125	99.9	97.8	98.2
250	100.0	100.0	100.0

Available lime was determined with the Franke method as indicated in normative EN459-2 [3]. The TG/DSC analyses were carried out in the 25–1000 °C temperature range with a heating rate of 20 °C/min in a nitrogen/air atmosphere, with a STA 409PC Luxx Netzsch instrument (as an example, see the TG/DSC analysis of sample 1 in Fig. 1). Particle size analysis was accomplished with a Coulter LS 230 laser granulometer, used in the dry module.

3. Results and discussion

As reported in Table 2, the three samples have similar grain-size distribution. Table 3 reports the chemical composition of the hydraulic limes used in this study and Table 4 the CaO content using the Franke method. As pointed out by Callebaut et al. [4], chemical data alone are insufficient for an accurate characterization of the hydraulic properties of hydraulic limes. Nevertheless, chemical analyses have been for long time the only reliable data available to cement chemists. Thus, many indexes, based on oxides composition of cement materials, have been defined to quantify their hydraulic properties. For hydraulic limes, the cementation index (CI) has been reported by Boynton [12] as (Eq. (4)):

$$\mathrm{CI} = \frac{(2.8\%\mathrm{SiO_2} + 1.1\%\mathrm{Al_2O_3} + 0.7\%\mathrm{Fe_2O_3})}{(\%\mathrm{CaO} + 1.4\%\mathrm{MgO})} \qquad (4)$$

Limes showing CI within 0.3 and 0.5 were defined weakly hydraulic, for CI values between 0.5 and 0.7 moderately hydraulic, for CI values between 0.7 and 1.1 highly hydraulic. Following these rules, samples 1 and 2 are classified as highly hydraulic, while sample 3 as moderately hydraulic (see Table 3). The latter showing less SiO_2 and Al_2O_3, and more CaO.

Table 3
Chemical analyses of the hydraulic lime samples

Oxides	1 (%)	2 (%)	3 (%)
SiO_2	15.6	18.8	12.5
Al_2O_3	4.40	2.65	1.36
Fe_2O_3	2.32	0.93	0.45
TiO_2	0.19	0.12	0.06
CaO	49.3	56.1	63.3
MgO	1.57	2.31	1.51
Na_2O	0.27	0.15	0.12
K_2O	1.19	0.47	0.20
SO_3[a]	2.60	1.55	0.80
L.O.I.	22.2	16.6	19.3
Total	99.64	99.68	99.60
C.I.	0.91	0.95	0.56

[a] SO_3 determined by gravimetric method.

Table 4
Available lime (Franke method) expressed as CaO%

Sample	CaO (%)
1	0.17
2	16.5
3	32.4

This conclusion can be drawn also looking at the quantitative phase analysis (QPA) whose agreement factors were all pretty low ($R_{wp}<0.13$ and $\chi^2<5$, see also an example of fit in Fig. 2) reported in Table 5, where it can be appreciated the relative high content in calcium silicates for all the samples, with sample 3 showing higher amount of portlandite. Other peculiar characters of the chemistry can be interpreted looking at phase composition. The high iron content of sample 1 is coherent with its classification as hydraulic lime HL5, and, as shown in Table 5, here is present C_4AF, that can accommodate most of the available iron. Similarly, the high magnesium content of sample 2 is in accordance with the presence of periclase, since under 1450 °C, in systems containing significant amounts of MgO, segregation of large periclase crystals occurs [5]. Of course, magnesium, iron, and other minor elements, normally enter as impurities at various level in many phases. This means that a comparison between instrumental chemical analyses and chemical analyses inferred from the quantitative XRPD data, using the stoichiometric composition of crystalline phases, cannot be drawn without relevant errors. Furthermore, in systems containing an amorphous component, this procedure cannot be applied.

From these observations, it follows that a correct classification of this class of products should take into consideration also their phase composition in conjunction with the chemical parameters. In fact, the reactivity towards water depends upon the nature and weight fraction of the

Table 5
Quantitative phase analyses of the hydraulic lime samples, errors in parenthesis

Phases	1[a] (%)	2[a] (%)	3 (%)
C_3S	11.6(2)	4.2(2)	2.5(3)
C_2S	9.0(3)	30.1(1)	24.1(2)
C_3A	n.d.	n.d.	1.4(2)
C_4AF	2.2(4)	–	–
Calcite	46.9(1)	22.8(2)	16.3(2)
Dolomite	1.3(3)	–	–
$Ca(OH)_2$	–	19.3(2)	42.0(2)
Quartz	4.2(3)	5.1(4)	2.8(3)
Gehlenite	–	1.2(3)	0.6(2)
Periclase	–	1.3(3)	–
Anhydrite	1.5(3)	1.1(3)	–
Gypsum	2.2(3)	–	–
Amorphous	21.3(2.2)	14.9(2.0)	10.1(1.6)

[a] Samples 1, 2, containing also C_3A.

Table 6
Determination of CO_2 expressed as calcium carbonate by calcimetric method and TG/DSC

Sample	$CaCO_3$ calcimeter (%)	$CaCO_3$ TG/DSC (%)	$CaCO_3$ Rietveld (%)
1	47.1	47.3	46.9
2	23.3	22.9	22.8
3	16.5	17.2	16.3

Calcite determination with the Rietveld method added for comparison.

phases present in the sample. QPA is more important for hydraulic limes with respect to cements, because the former show a not negligible amount of an amorphous phase whose chemical nature is not known.

Table 4 shows the values of available lime, expressed as CaO%. The determination of available lime with the Franke method is actually a measure of the calcium content of lime and portlandite. Samples 2 and 3 show higher values of total CaO but lower values of calcite than the sample 1. This means that in these samples, the available CaO for reaction in higher than the corresponding on sample 1, where the quantity of CaO is associated with calcium carbonate.

As reported in Table 5, in the hydraulic lime HL5, portlandite and free lime are absent, accordingly with the very low value of available lime determined (0.26%). It is worth saying that, for very low content (less than 0.5%), CaO cannot easily be quantified by XRPD, due to a strong peak superimposition with other silicates. The values of available lime that can be derived from the amount of $Ca(OH)_2$ found in samples 2 and 3 are 14.6% and 31.8%, respectively. If the latter value can be considered in good agreement with the result of the chemical analysis, the same cannot be said for the former. One reason for this underestimation (of about 2%) could be the low degree of crystallinity of portlandite, often observed in cement materials [13], yielding a marked broadening of the diffraction peaks. The profile parameters found during our refinements imply very small crystallite sizes, indicating that at least a fraction of $Ca(OH)_2$ could be completely amorphous. This means that, in part, what was measured as calcium hydrate by chemical analyses, is not detected as portlandite by XRPD, being instead calculated as amorphous. The real extent of this phenomenon would be revealed elucidating the nature of the amorphous phase.

In Table 6 are reported the values of CO_2, expressed as calcium carbonate, obtained by calcimetric method for the three samples studied, and the carbonate content, expressed as calcium carbonate, obtained by TG/DSC. Comparing these values with those obtained from the Rietveld method, we can observe that all data are in good agreement indicating a good accuracy of the QPA performed with the Rietveld method.

As observed, sample 1 shows the absence of portlandite and free lime, but also the highest calcium carbonate content. This could be the result of sample deterioration, eventually caused by a long storage period, but the different nature of the sample undoubtedly play an important role. As previously discussed, in NHL C_2S is more abundant than C_3S, the C_2S/C_3S ratio depending mainly upon the operating conditions of the kiln. This ratio furnishes also the easiest way to distinguish NHL from HL, since the “cementitious” nature of the latter, more like that of conventional cements, is characterized by an higher amount of C_3S with respect to C_2S. This can be easily seen by comparing the quantitative results for sample 1 with those obtained for samples 2 and 3 (Table 5).

Sample 1 shows the highest amount of calcite and C_3S as well as the highest CI compared with the other samples. Even though this sample does not contain free lime capable of reacting with silico-aluminates, it shows the highest CI

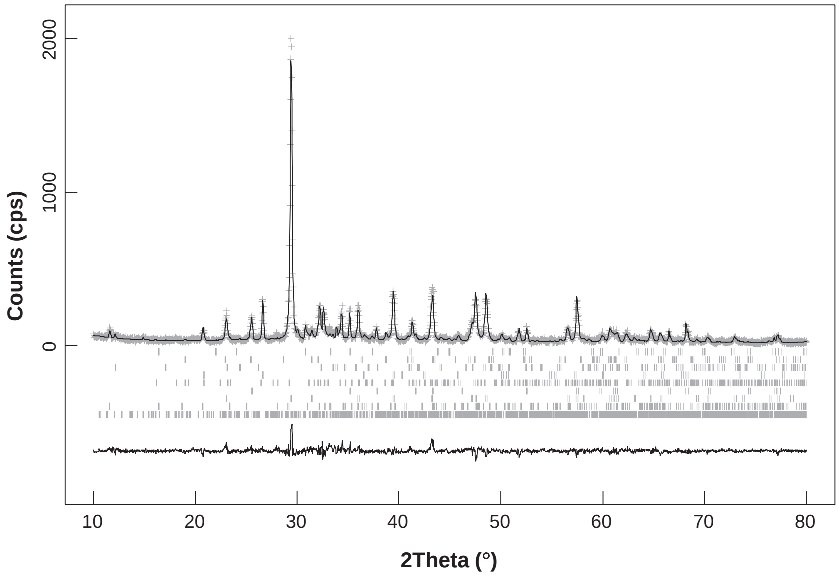

Fig. 2. Observed (crosses) and calculated (single line) powder diffraction patterns for sample 1 in the angular range 10–80 °2θ. Vertical bars mark Bragg reflection positions; from top to bottom: dolomite, anhydrite, C_4AF, quartz, C_2S, corundum, calcite, gypsum, C_3S. Difference curve on the bottom.

and the highest amount of C_3S. It is known that C_3S hydrates faster than C_2S contributing more to the hydraulic character. However, the high contents of C_2S and $Ca(OH)_2$ measured in the sample 2 and 3 will enhance their hydraulicity. The $Ca(OH)_2$, e.g., can be transformed to $CaCO_3$ and/or react with some of the amorphous phase to form further hydraulic compounds. In the amorphous phase, it is expected that the clay minerals will be included with destroyed crystallographic structures after heating, capable of reacting with calcium hydrate [14].

From these observations, it becomes evident that the CI calculated from the chemical analysis cannot unambiguously express the level of hydraulicity. The applied formula for the calculation of CI does not make any distinction between available CaO and SiO_2 for reaction and their corresponding total amounts. This information can only be obtained from the Rietveld-RIR method, thus giving good reason for its use for the classification of hydraulic limes and performing quality control.

Other indices could probably be defined, using the QPA data, to emphasise the differences between HL and NHL (considering also calcite and portlandite), or to express the "hydraulicity" of these materials, but this would require further investigations that are beyond the scope of this work.

It should be emphasised that, in order to achieve good accuracy results, the QPA of hydraulic limes with the Rietveld method must be conducted with the internal standard. In fact, it is not possible to exclude the presence of the amorphous phase a priori. The inspection of the powder diffraction pattern is of no help, since even high amounts often do not produce any recognisable deformation in the background (see Fig. 2). If we take sample 1 as an example, a QPA performed without internal standard, implies that a weight fraction of 21.3 wt.% will be proportionally distributed between the crystalline phases, invariably leading to large errors.

4. Conclusions

Application of the Rietveld method to phase quantification of production hydraulic lime samples is very promising. Results of calcium carbonate content are in good agreement with those obtained from the traditional gas-volumetric (calcimetric) method and TG/DSC. Hydraulic limes, classified as HL, and natural hydraulic limes, NHL, can be easily identified thanks to their different C_2S/C_3S ratio. Some peculiar chemical characteristic can be interpreted in the light of the appearance or disappearance of mineral components, even though the direct comparison between chemical analyses and chemical analyses inferred from the quantitative XRPD data, using the stoichiometric composition of crystalline phases, is prevented by the presence of some amorphous material, and by the non-stoichiometry of most phases. The systematic slight underestimation of available lime derived from the quantitative assessment of portlandite, together with its low degree of crystallinity, suggested that at least a fraction of $Ca(OH)_2$ could be completely amorphous and consequently not directly detectable by XRPD.

It should be noted that, for practical applications, time and conditions of conservation may considerably alter the hydraulic properties of the product, leading to high differences between the expected phase composition and the real one. XRPD is a very powerful tool for a complete characterization of such industrial products, but, in order to be exploited correctly, measurement conditions should be carefully chosen, and internal standard must be employed.

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