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# Direct determination of total carbonate salts in soil samples by continuous-flow piezoelectric detection

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## Abstract

Two new methods for the determination of total carbonate salts, as $CaCO_3$, in soil by continuous-flow piezoelectric (PZ) detection are proposed. Both use a piezoelectric flow cell and a manifold including a dynamic gas extraction device to purge gaseous $CO_2$ released by the sample solution upon acidification. One of the methods involves monitoring the pressure generated by the $CO_2$ produced upon addition of hydrochloric acid; in the other, the $CO_2$ is quantified by using a quartz crystal coated with tetramethylammonium fluoride tetrahydrate (TMAF). The precision of both methods is compared with that of the officially endorsed method. The proposed methods allow calcium carbonate amounts over the ranges 10–100 mg and 2–15 mg, respectively, to be determined. Both were applied to the determination of $CaCO_3$ in soil samples. The standard deviation and throughput achieved were 2.7% and 30 samples per hour, respectively, with the pressure-based method; and 6.0% and six samples per hour, respectively, with the mass-based method.

*Keywords:* Piezoelectric sensor; Flow systems; Total carbonate; Soil samples

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## 1. Introduction

Soil properties play a major role in planning land use activities such as agriculture, erosion control, environmental protection and nature conservation. The determination of total carbonate salts such as $CaCO_3$ in soil is of great interest on account of its high usefulness for diagnosing soil status in terms of structure, texture, biological activity or nutrient contents, among other characteristics. The determination of total carbonates ($CaCO_3$, $MgCO_3$, etc.), expressed as percentage $CaCO_3$, is based on the volumetric analysis of the carbon dioxide released upon addition of an acid such as HCl or $HClO_4$ to soil carbonates. The release of carbon dioxide, and hence the presence of carbonate in soils, is signalled by foaming during application of the acid.

Spain's Ministry of Agriculture, Fisheries and Food [1] currently endorses two methods for determining soil carbonates. One is based on the Bernard calcimeter [1] and has retained its first action classification since 1952. This method, however, is poorly sensitive and rather complicated as all measurements have to be made under the same conditions in order to avoid the effect of differences in temperature or pressure. The other method is of the volumetric type [1] and involves the addition of perchloric acid to the soil, followed by titration with sodium hydroxide; the procedure is rather time-consuming.

There are few reported instrumental methods for routine soil analyses. Piezoelectric (PZ) crystals are known to be quite sensitive to pressure and mass changes on their surfaces; these properties enable their use in quantitative trace analysis [2]. In fact, the use of PZ quartz crystals for the detection of gaseous compounds has become increasingly popular [3,4] since their earliest application in this area was reported [5]. These devices are often called "quartz crystal microbalances" (QCMs). Usually, the quartz crystal is sandwiched between two electrodes that are then coated with a substrate capable of absorbing the compounds to be measured. Any increase in mass or pressure on the surface of

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the crystal will result in a decrease in vibrational frequency conforming to the equation of Sauerbrey [6]

$$\Delta F = -\frac{2\Delta m F^2}{A(\rho\mu)^{1/2}} \qquad (1)$$

where $\Delta F$ is the change in resonant frequency, $\Delta m$ that in mass, $F$ the fundamental resonant frequency of the device, $\rho$ the density of quartz (2.65 g cm$^{-3}$), $\mu$ the shear modulus of the crystal ($2.95 \times 10^{11}$ dyne cm$^{-2}$) and $A$ (0.20 cm$^2$) the surface area of the electrode. The sensitivity of a QCM depends mainly on the thickness of the crystal. In previous work [7], a frequency change of 1 Hz was found to correspond to a mass increase of 1.05 ± 0.01 ng on the QCM electrode, consistent with the following expression

$$\Delta F = -[(1.05 \pm 0.01) \times 10^{-9}]\Delta F \qquad (2)$$

which can be derived from Eq. (1).

Upon coating with a material capable of selectively absorbing gaseous species, the crystal can be used as a monitoring device, the sensitivity of which will depend on the coating/analyte area, temperature and molar reaction ratios, and its response time on the reaction kinetics (which in turn will be influenced by the gas flow rate, rate of presentation of the analyte gas sample to the coating, temperature and analyte concentration) [8]. Coating materials that are stable, free from aging (through oxidation or hydrolysis) under atmospheric conditions, and reactive towards specific gases, and possess good reversibility properties, continue to be the best choices for dynamic real-time trace gas analysis. King [9,10] reported the first use of a coated piezoelectric crystal in gas chromatography; by developing a detector sensitive to 0.1 ppm water. The coating materials tested as water sorbents include molecular sieves, hygroscopic polymers, silica gel, polar liquids, gold, nickel and aluminum. Guilbault and López Román [11] found the frequency response of PZ crystals to increase with increasing temperature (especially over the range 100–200 °C); between 25 and 40 °C, however, the effect of temperature was very weak. This work was completed before their investigation of the use of the following coating materials for detecting sulfur dioxide: sodium tetrachloromercurate, apiexon, silicone, SE-30, silicone QF-1, Carbowax 20 M and Versamid 900.

Liquid coatings can be applied to crystals in a variety of ways including dropping, smearing, dipping, spraying, and spinning. Dipping allows no control over deposition. Smearing is time-consuming and, since the control parameter is the frequency, it is possible to have different amounts of coating unevenly spread over the electrodes. Finally, spin coating is rarely used.

A number of analytical uses of piezoelectric quartz crystals have recently been reported. Thus, Zhao et al. [12] used one sandwiched between gold electrodes and coated with a sensitive membrane of chitosan to detect and quantify volatile amines. These compounds can also be determined with uncoated PZ crystals sandwiched between gold electrodes [13]. Our group has used this approach for various other analytical purposes [14–16].

The quartz crystal microbalance provides a sensitive, inexpensive means for the detection and quantitation of small amounts of $CaCO_3$. In fact, coated crystals have previously been used to detect $CO_2$ [17]. However, uncoated PZ crystals sandwiched between gold electrodes can also be used with soil samples in order to avoid problems arising in the application of coatings (e.g. non-uninformity, irreproducibility) and changes through evaporation or uncontrolled spreading during coating. Amines are widely used industrially to absorb $CO_2$. Thus, *N*,*N*,*N*,*N*′-tetrakis(2-hydroxyethyl)ethylenediamine (THEED) has been used to coat PZ quartz crystals with a view to determining carbon dioxide [18,19]. The THEED coating reacts reversibly with $CO_2$, which increases its sorption frequency. However, the resulting calibration graphs are of limited use, probably as a result of spreading of the liquid coating on the crystal surface [20].

In this work, we used uncoated and tetramethylammonium fluoride tetrahydrate (TMAF) coated crystals to quantify $CaCO_3$ in soil. This particular coating material was chosen on the grounds of its high $CO_2$ sorption capacity and the fact that gas absorption and desorption in it are fully reversible and temperature-dependent [21,22].

## 2. Experimental

### 2.1. Reagents

The coating agent TMAF, was purchased from Aldrich and dissolved in ethanol. Silica gel, also from Aldrich, was used to dry $CO_2$ released upon the addition of hydrochloric acid (35%, Panreac) to calcium carbonate (Merck). The nitrogen used was reagent-garde N45 from Air Liquid.

### 2.2. Crystal coating

The piezoelectric crystals used were coated on both faces with 1% (w/v) solutions of TMAF in absolute ethanol, using the spraying method of Quinn et al. [22]. The choice of TMAF as coating material was based on previous results [23,24] that testified to its high absorption sensitivity for $CO_2$. Before and after application of TMAF, the quartz crystal was accommodated in a flow cell and the resonant frequency of the sensor measured with a Hewlett-Packard HP-34912A/225 frequency counter. The average frequency for the coated sensors (viz. those assumed to have been coated by TMAF) was 9,913,200 Hz, whereas that for the uncoated sensors was 9,985,657 Hz; this allowed the average amount of TMAF deposited onto the crystals to be determined.

### 2.3. Apparatus

The crystals used were AT-cut 10 MHz specimens with gold plated electrodes 0.17 mm thick and 14 mm in diameter. Prior to use, the crystals were washed with 2 ml of “piranha” solution for about 1 min. This was followed by rinsing with distilled water, ultrasonic cleaning in distilled water for 5 min, rinsing with distilled water and absolute ethanol several times, and drying in a nitrogen stream. The clean, dry crystals were then placed in a measuring chamber and allowed to resonate for 5 min. Each quartz crystal was accommodated in a laboratory-made flow cell and its resonant frequency measured with a Hewlett-Packard HP-34812A/225 frequency counter connected to a Pentium PC computer via an HP–IB interface (also from Hewlett-Packard). Data were acquired and stored using HP-34812A BenchLink software (HP BenchLink/Meter). A Gilson Minipuls-3 peristaltic pump and a Rheodyne 5301 three-way injection valve were also used.

### 2.4. Manifold design and procedure

Fig. 1a depicts the laboratory-made flow cell used in this work. It consisted of a polyethylene cylinder 7.0 cm long and 3.5 cm in diameter one end of which was fitted with a lid that allowed the position of the crystal to be inspected and changed, if necessary. Two connectors located 3.5 cm from the lid allowed the gas flow to be split and the two resulting streams to be led to the center of each crystal face. The mass-based method (Fig. 1c) made no use of one opening, which was thus sealed with a stopper. In such a method, the frequency shift was found to decrease with decreasing distance between the crystal face and the connector that allowed the gas flow to be split. This frequency decrease shift has

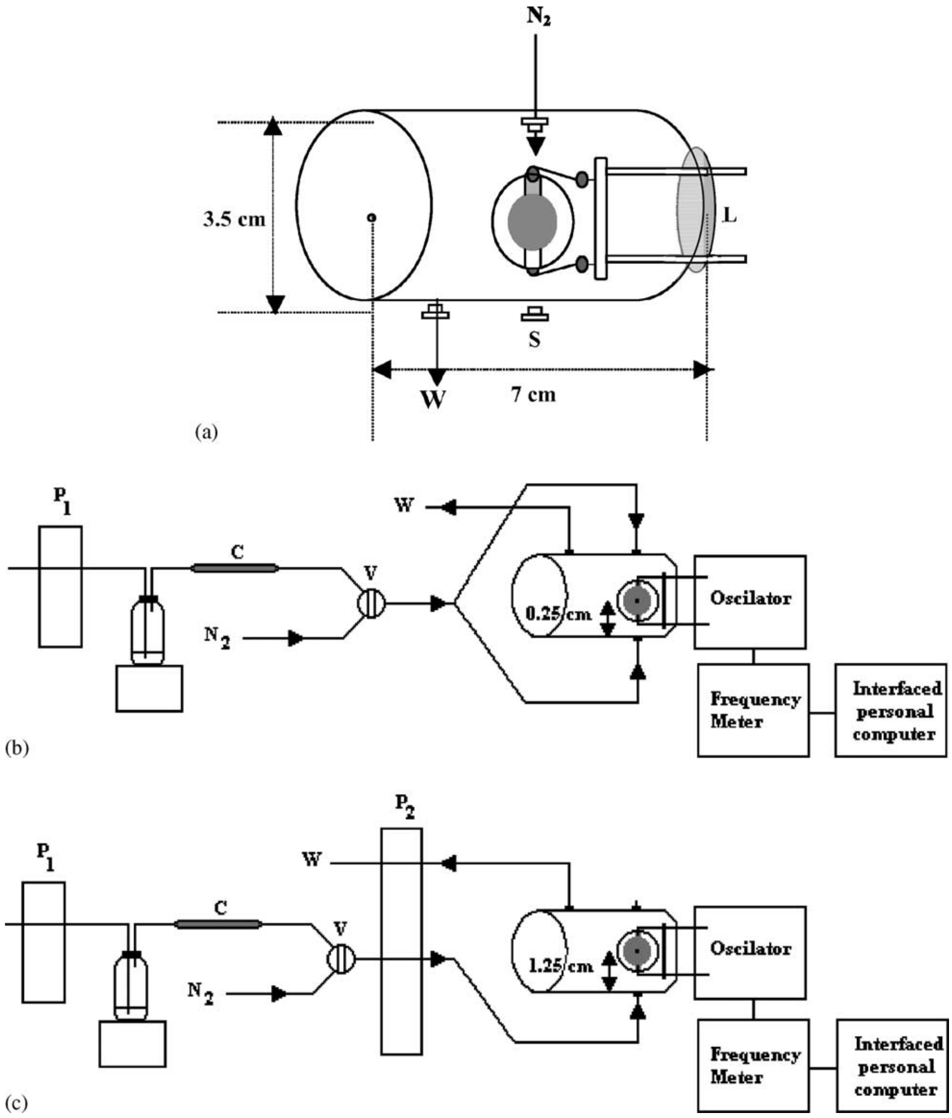

Fig. 1. Detection system. (a) Flow cell for the quantitation of $CaCO_3$ in soil samples. (b) Pressure-sensitive detector. (c) Mass-sensitive detector. $P_1$, $P_2$ peristaltic pumps; V switching valve; C silica gel column; W waste; L Lid; S stopper.

Table 1
Frequency shifts observed in the uncoated and coated crystals in the determination of 50 and 10 mg, respectively, of $CaCO_3$ at variable distances between the connectors splitting the gas flow and the centre of the crystal face

| Distance (cm) | Frequency shift (Hz) | |
|---|---|---|
| | Uncoated crystal | Coated crystal |
| 1.75 | 130 | 250 |
| 1.25 | 158 | 255 |
| 0.75 | 170 | 175 |
| 0.50 | 193 | 100 |
| 0.25 | 220 | 75 |

no easy explanation. It may have resulted from the difficulty of absorbing $CO_2$ at short distances. In the pressure-based method, the frequency shift was maximal when the crystal was 0.25 cm from the lower connector (see Fig. 1b). Based on the data of Table 1, the maximum frequency signals were obtained with a distance of 0.25 cm for uncoated crystals and 1.25 cm for coated crystals. Fig. 1b and c show the manifolds used. In order to measure frequency shifts, nitrogen was fed into the detector at room temperature (20 °C) until a stable frequency was obtained. Then, the switching valve (SV) was actuated to have the peristaltic pump ($P_1$) propel 4.0 ml of 50% HCl into a 5 ml vessel containing a sample thermostated at 20 °C at a flow rate of 4 ml $min^{-1}$ for exactly 1 min in order to remove calcium carbonate as $CO_2$ gas. The process was facilitated by magnetically stirring the suspension inside the vessel. The $CO_2$ thus released was dried over silica gel and passed through a piezoelectric flow cell (PZ-FC), where the signal was detected, transferred to the frequency counter (*F*) and recorded (PC). The $CO_2$ released by both samples and calibration standards was injected into the flow cell once the baseline resonant frequency ($F_b$) had levelled off. Measurements were in the form $\Delta F = |F_p - F_b|$, where $F_P$ denotes the maximum frequency during each run.

The pressure-based method relies on pressure measurements of the $CO_2$ released by the $CaCO_3$ contained in the soil samples. The baseline frequency was established by using $N_2$ at a flow rate of 25 ml $min^{-1}$. The mass-based method quantifies $CO_2$ absorbed in the coated crystal; the flow rate at which the gas was passed through the flow cell was adjusted to 18 ml $min^{-1}$ using the peristaltic pump ($P_2$) located in front of the flow cell holding the piezoelectric crystal. The waste was pumped at the same flow rate in order to ensure a constant flow rate and pressure in the flow cell. Once the frequency leveled off, the system was flushed with nitrogen. The desorption time following $CO_2$ uptake never exceeded 10 min.

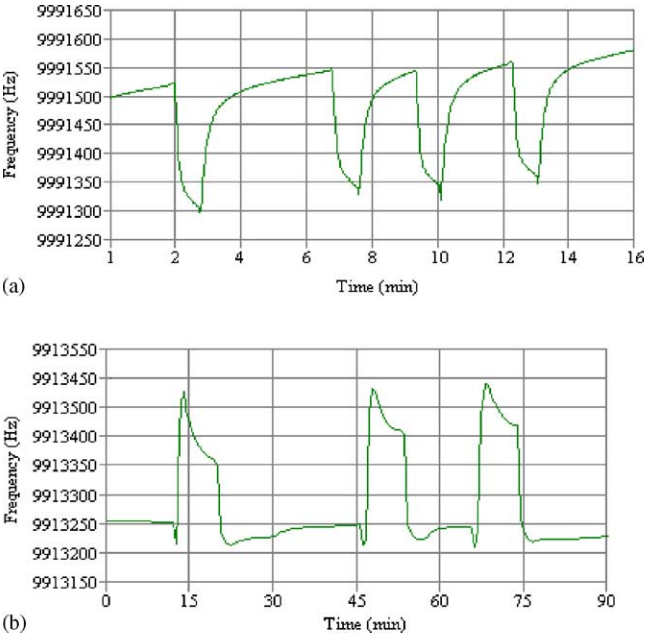

Fig. 2. Frequency change in (a) an uncoated crystal after a series of four injections for the determination of 50 mg of $CaCO_3$ at 20 °C and (b) a TMAF-coated crystal after a series of three injections for the determination of 10 mg of $CaCO_3$ at 20 °C.

## 3. Results and discussion

### 3.1. Pressure-based method

The response of the 10 MHz-cut quartz crystal was consistent with previous reports [25]. Thus, the frequency decreased on bringing one face of the crystal into contact with the passing $CO_2$ flow. Fig. 2a shows the frequency–time profile obtained for a series of four injections of 50 mg $CaCO_3$ each. As stated above, measurements were in the form of differences between the baseline frequency and the maximum frequency during each run. In this way, the frequency change was caused by varying the pressure over the quartz electrode surface and depended exclusively on the amount of $CaCO_3$ present. In fact, the frequency change (detector response) was linearly related to the volume of $CO_2$ passing through the piezoelectric flow cell. Standards containing 10–1000 mg of $CaCO_3$ were used to construct the calibration graph required to determine it. Table 2shows the figures of

Table 2
Figures of merit of the proposed methods, regression analysis ➔ linear model: $Y = a + bX$

| Method | $a \pm S_a$ | $b \pm S_b$ | Regression coefficient | Determination range (mg) | Throughput (samples per hour) | Limit of detection (mg) | Precision (% R.S.D.) |
|---|---|---|---|---|---|---|---|
| Uncoated crystal | 62.9167 ± 4.3586 | 2.7634 ± 0.0772 | 0.9953 | 10–100 | 30 | 6.75 | 2.67 |
| Coated crystal | 1.5991 ± 7.3138 | 19.6959 ± 0.7767 | 0.9938 | 2–15 | 6 | 1.11 | 6 |

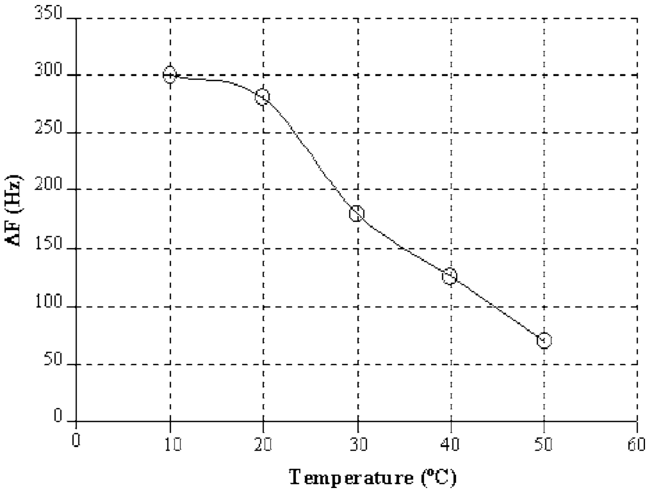

Fig. 3. Effect of temperature on the frequency shift caused by an amount of $CaCO_3$ of 10 mg.

Table 3
Stability of the TMAF-coated crystal

| Day | Frequency (Hz)[a] | $\Delta f$ (Hz) ± R.S.D. (%)[b] |
|---|---|---|
| 1 | 9,913,250 | 275 ± 6.1 |
| 2 | 9,913,210 | 292 ± 3.2 |
| 4 | 9,913,354 | 284 ± 4.7 |
| 7 | 9,913,327 | 278 ± 2.9 |
| 10 | 9,921,251 | 264 ± 3.4 |
| 13 | 9,929,872 | 254 ± 4.5 |
| 14 | 9,937,368 | 258 ± 5.2 |
| 16 | 9,945,897 | 175 ± 6.1 |
| 18 | 9,957,581 | 154 ± 4.9 |
| 19 | 9,961,574 | 135 ± 7.7 |
| 21 | 9,967,140 | 120 ± 8.5 |

[a] Frequency of the TMAF-coated crystal.

[b] Frequency shift observed in the TMAF-coated crystal upon injection of 10 mg of $CaCO_3$.

merit of the proposed method. The calibration graph, which was run from triplicate measurements at each point, was linear over the range 10–100 mg. The precision of the method, as the relative standard deviation for 50 mg of $CaCO_3$, was ±2.67 ($n = 10$). The limit of detection, which was taken to be the mass of $CaCO_3$ giving a signal equivalent to three times the standard deviation for the blank signal plus the net blank intensity, was 4.73 mg. The throughput was estimated to be 30 samples per hour.

## 3.2. Mass-based method

### 3.2.1. Response of the coated crystal to $CO_2$

Fig. 2b shows typical responses ($\Delta F$) of the TMAF-coated crystal to $CO_2$ in a series of three determinations of 10 mg of $CaCO_3$ at room temperature (20 °C). Upon exposure of the crystal to $CO_2$ gas, which caused a frequency shift, the frequency changed (in a rapid manner first and more slowly then) until it leveled off —which occurred within 10 min. The desorption time after $CO_2$ uptake never exceeded 10 min, which can be acceptable for a sensor. The time-dependent signal provided by the crystal, $\Delta F$, increased with increase in the amount of $CaCO_3$ over the range 2–25 mg. Consistent with previous findings of Quinn et al. [26], the unusual shape of the signals (particularly their abrupt frequency rise) can be ascribed to liquefaction of the $CO_2$ absorption product.

### 3.2.2. Effect of temperature

The response of the coated crystal to 10 mg of $CaCO_3$ at variable temperatures from 10 to 50 °C was monitored. As can be seen from Fig. 3, the crystal response to $CO_2$ absorption decreased with increasing temperature; also, large temperature differences proved detrimental to the determination of $CaCO_3$. The resonant frequency increased markedly relative to air above 40 °C. This can be ascribed to the loss of TMAF membrane coating. Clearly, the coating was affected by temperature, but not by $CO_2$ sorption. We thus adopted a temperature of 20 °C for the determination of $CaCO_3$ in soil samples.

### 3.2.3. Service lifetime and repeatability of the coated crystal

For the coated crystal to be useful in practice, it should have a long lifetime and a high repeatability. Table 3 shows the frequency of the TMAF-coated crystal and the frequency changes observed in the determination of 10 mg of $CaCO_3$ in a nitrogen stream at a constant flow rate. As can be seen, the TMAF coating was stable for 2 weeks; between-day differences in frequency shift were not significant and variations in crystal frequency were very small. After 2 weeks, the crystal frequency started to increase with time and the frequency shifts observed in the determination of 10 mg of $CaCO_3$ were too small owing to evaporation of the coating membrane.

### 3.2.4. Figures of merit of the proposed method

The proposed method provided analytical graphs run from triplicate measurements at each point that were linear over the range 2–15 mg $CaCO_3$. A typical equation, $A = (1.5991 \pm 7.3138) + (19.6959 \pm 0.7767)[CaCO_3]$, with a regression coefficient of 0.9938, was obtained. The signal appeared 2 s after the sample was injected and the $F_1$ manifold was ready for a new injection within 10 min. The throughput was thus about six samples per hour. The precision of the method, as the relative standard deviation for 10 series of 10 replicate measurements each, was 6% for 10 mg of $CaCO_3$. The limit of detection, defined as the mass of $CaCO_3$ giving a signal equivalent to three times the standard deviation of the blank plus the net blank intensity, was 1.1 mg.

Table 2 shows the figures of merit of the proposed method. As can be seen, the pressure-based method provided a broader determination range, better precision and a higher throughput, but also a lower sensitivity.

Table 4
Analysis of soil samples containing $CaCO_3$ ($n = 3$)

| Sample | Oficial (%) | Uncoated crystal | | Coated crystal | |
|---|---|---|---|---|---|
| | | Found (%) | Difference ($d$)[a] | Found (%) | Difference ($d$)[a] |
| Soil 1 | 9.8 ± 1.0 | 9.5 ± 0.5(0.5 g)[b] | −0.3 | 10.1 ± 0.2(0.1 g) | 0.3 |
| Soil 2 | 7.3 ± 0.3 | 7.4 ± 0.5(0.5 g)[b] | 0.1 | 7.7 ± 0.4(0.1 g) | 0.4 |
| Soil 3 | 4.3 ± 0.2 | 3.9 ± 0.4(0.5 g)[b] | −0.4 | 3.8 ± 0.1(0.1 g) | −0.5 |
| Soil 4 | 1.75 ± 0.05 | 1.5 ± 0.2(1 g)[b] | −0.25 | 1.7 ± 0.1(0.1 g) | −0.05 |
| Soil 5 | 0.60 ± 0.02 | n.d[c] (1 g)[b] | – | 0.7 ± 0.1(0.1 g) | 0.1 |

[a] Difference ($d$) = proposed method − official method.
[b] Weight of soil samples.
[c] Not detected.

## 4. Analysis of real samples

The practical usefulness of the proposed methods was assessed by using the coated crystal to analyse soil samples containing small amounts of calcium carbonate and the uncoated crystal with samples containing large amounts of analyte. The samples also contained small amounts of organic matter and $MnO_2$. The two methods were also compared with the reference analytical method [1] for this type of sample. As can be seen from Table 4, the results obtained with both proposed methods were consistent with those provided by the reference method. A paired $t$-test revealed the absence of significant differences with it. Thus, the computed $t$ statistic for the pressure-based method, 1.18, was smaller than the tabulated $t_{\text{crit}}$ value (viz. 3.18 for 3 d.f. at the 95% confidence level). There was thus no evidence of the presence of systematic errors in the results. The pressure-based method was thus chosen to determine $CaCO_3$ in soil samples containing large amounts of analyte. The computed $t$ statistic for the mass-based method, 0.88, was also smaller than the tabulated $t_{\text{crit}}$ value (viz. 2.78 for 4 d.f. at the 95% confidence level); therefore, the method was adopted for the determination of $CaCO_3$ in soil samples containing small amounts of analyte.

Potential interferences with the determination of the analyte in samples with high organic matter of $MnO_2$ contents can be minimized by adding a reductant (e.g. $FeCl_2$) to the HCl solution. This shortens the reaction time or destroys organic matter. The potentially interfering effects of $H_2S$, $SO_2$ and $NH_3$ released upon acidification can be avoided by using a zeolite trap to allow the selective detection of $CO_2$ in a mixture with the other gases [27].

## 5. Conclusions

Piezoelectric quartz crystals enable inexpensive, highly sensitive analytical determinations. However, they have scarcely been applied to real samples. In this work, we developed two fast, straightforward, sensitive methods for quantifying calcium carbonate in soil samples. The mass-based detection method is time consuming owing to the need for $CO_2$ to be desorbed from the coating membrane. Also, the sensor has a limited lifetime. In any case, the method can be practical for determining small amounts of $CaCO_3$. By contrast, the pressure-based detection method is affordable and easily implemented even with laboratory-made equipment; also, it avoids the above-described problems inherent in the use of coated sensors.

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