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# Polyethylene Spray Bottles as Weighing Burettes

## Titrimetric Determination of Calcium Carbonate in Limestone, Cement Raw Mixtures, *etc.*

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A quick and accurate method of titration by weight which does not call for extra (possibly automatical) titration equipment has been developed.

The method introduces the use of polyethylene spray bottles as weighing burettes. (The inside diameter of both ends of the spray nozzle has been reduced to about 0.5—1 mm, in order to diminish the size of the drops.) These spray bottles can be handled by hand without any protection, because the weighing inaccuracy which thus appears in comparison with the essential factor of inaccuracy — the drop size — is of no consequence.

The method has been tried out in acid-base titration of the calcium carbonate content of limestone and cement raw mixtures, resulting in a standard deviation $s = 0.05$ % $CaCO_3$. When a limestone containing 80 % $CaCO_3$ is titrated, this corresponds to a coefficient of variation of 0.06 %.

The time required for carrying out an analysis is the same as in ordinary burette titration.

As the use of polyethylene spray bottles as weighing burettes has not been described previously in the literature, the principle will be accounted for in the following description of its application in acid-base titration of calcium carbonate in cement raw mixtures, but the general principle can, of course, be applied to other titrations.

200 ml or 250 ml polyethylene spray bottles are used, with shortened spraying nozzles (inside diameter of tip: 0.5—1 mm), so that bottle with spraying nozzle is not higher than about 15 cm (in order to fit the balance pan). The spraying nozzle is sealed on the holder of the bottle lid with glue, making the bottle airtight when the lid is screwed on firmly.

For the NaOH solution which is used in the back-titration, a spray bottle is employed where the end of the spraying nozzle inside the bottle has been extruded so that the inside diameter of the nozzle is 0.5—1 mm on a length of about 4 cm (see Fig. 1). This ensures that a slight pressure on the side of

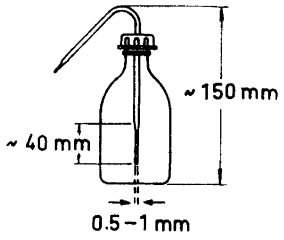


*Fig. 1.* Polyethylene weighing burette for NaOH solution. Over a length of 4 cm, the end of the spraying nozzle inside the bottle is extruded to an inside diameter of 0.5—1 mm.

the bottle will make the liquid column remain in the spraying nozzle, and that a small increase of the pressure will make the liquid leave the tip of the spraying nozzle in small drops (see Table 1).

*Table 1.* Importance of diameter of that part of the spraying nozzle which is inside the spray bottle.

| Weight of drop from extruded spraying nozzle, 0.5—1 mm diam. (Fig. 1). | Weight of drop from ordinary spraying nozzle, ~5 mm diam. |
|---|---|
| $V_u$ (g) | $V_o$ (g) |
| 0.0108 | 0.0180 |
| 0.0130 | 0.0185 |
| 0.0110 | 0.0185 |
| 0.0100 | 0.0220 |
| 0.0105 | 0.0195 |
| $\overline{V}_u = 0.011$ ($s = 0.001$) | $\overline{V}_o = 0.019$ ($s = 0.002$) |

The time required for the back-titration with the NaOH solution is about 2 min, and in order to investigate the influence of the touch of the palm of the hand on the polyethylene bottle in this period, the following experiments were carried out:

The polyethylene spray bottle, filled with water, was weighed several times at intervals of 2 min. In these 2-min intervals the bottle was held in the hand with almost the same pressure as is used in the titration, but without any liquid being spilled. The weighings were repeated by several laboratory assistants, both without any protection and with silk as protection between bottle and palm. The results are shown in Table 2.

An F-test [1,2] on the result shows, to the 99 % confidence limit, no significant difference between the weighings with and without protection between bottle and palm, as long as the bottle is handled with dry, clean hands; nor is there any difference between the weighings of the laboratory assistants.

*Table 2.* Changes in weight of the weighing burette as a result of the handling.

| | Bottle touched with perspiring hands | Bottle touched with dry, clean hands | Bottle touched with protecting cover over hands |
|---|---|---|---|
| | $\Delta x_p$ (g) | $\Delta x_d$ (g) | $\Delta x_c$ (g) |
| Lab. ass. No. 1 | 0.0044 | 0.0004 | −0.0005 |
| | 0.0044 | 0.0002 | −0.0003 |
| | 0.0005 | 0.0001 | −0.0001 |
| | −0.0008 | 0.0001 | 0.0002 |
| | 0.0007 | 0.0004 | −0.0002 |
| | 0.0017 | −0.0002 | −0.0001 |
| | 0.0025 | −0.0001 | 0.0000 |
| | −0.0019 | 0.0000 | 0.0002 |
| | 0.0084 | −0.0001 | 0.0002 |
| | | 0.0005 | −0.0001 |
| | $\Delta\bar{x}_p = 0.0022$ ($s = 0.0025$) | $\Delta\bar{x}_d = 0.00013$ ($s = 0.00018$) | $\Delta\bar{x}_c = -0.00007$ ($s = 0.00014$) |
| Lab. ass. No. 2 | | 0.0000 | 0.0004 |
| | | −0.0004 | 0.0005 |
| | | 0.0004 | 0.0004 |
| | | −0.0001 | −0.0002 |
| | | −0.0004 | 0.0002 |
| | | 0.0002 | −0.0001 |
| | | 0.0003 | −0.0006 |
| | | −0.0003 | −0.0002 |
| | | 0.0000 | 0.0001 |
| | | 0.0002 | |
| | | 0.0005 | |
| | | −0.0005 | |
| | | −0.0001 | |
| | | $\Delta\bar{x}_d = -0.00002$ ($s = 0.00018$) | $\Delta\bar{x}_c = 0.00005$ ($s = 0.00018$) |

## METHOD

0.5 N hydrochloric acid and 0.25 N sodium hydroxide (standardized against $CaCO_3$ (Merck, a.p.)) are used for the titration, and phenolphthalein (2 % alcoholic solution) is used as an indicator. The sample to be analysed is weighed out in grammes to 5 decimals (using a Mettler B6 balance), the titrants are weighed out in grammes to 4 decimals (using a Mettler B5 balance).

### Standardisation of titrants

1. *Relative standardisation.* From a pre-weighed polyethylene spray bottle about 5 (*c*) g 0.5 N HCl solution are sprayed into a 150 ml beaker, after which the spray bottle is weighed again. The solution is diluted to about 80 ml, 2 drops of indicator are added, and back-titration (with simultaneous magnetic stirring) is done with 0.25 N NaOH solution (using *d* g) from a pre-weighed polyethylene spray bottle until incipient red-staining. The spray bottle is weighed again immediately after titration. The relative

standardisation indicates: grammes of 0.5 N HCl solution consumed per 1.0000 g 0.25 N NaOH solution ($e=c/d$).

2. *Standardisation of the HCl Solution.* 0.25 ($A$) g $CaCO_3$ (Merck a.p.) (previously dried for 45 min at 110°C) is weighed into a 150 ml beaker. From a pre-weighed polyethylene spray bottle about 15 ($a$) g 0.5 N HCl solution are added, and the spray bottle is weighed again. The solution is diluted to about 80 ml, and $CO_2$ is expelled by cautious boiling for 3 min (cover beaker with a watch glass). After cooling to room temperature, 2 drops of indicator are added, and the solution is back-titrated (with simultaneous magnetic stirring) with 0.25 N NaOH solution (using $b$ g) added from a pre-weighed polyethylene spray bottle until incipient red-staining. The spray bottle is weighed again immediately after titration. The HCl standardization indicates: $B$ g of $CaCO_3$ consumed per 1.0000 g 0.5 N HCl solution ($B=A/(a-be)$).

## Analysing procedure

0.25 ($G$) g of a previously crushed ($<90$ $\mu$) and dried (45 min at 110°C) sample is weighed into a 150 ml beaker. From a pre-weighed polyethylene spray bottle about 12 ($f$) g 0.5 N HCl solution are added, and the spray bottle is weighed again. Dilution, $CO_2$ expulsion and back-titration (using $g$ g) are carried out as described under the HCl standardisation. Based on the quantities by weight of 0.5 N HCl solution and 0.25 N NaOH solution added, the calcium carbonate content of the sample can easily be calculated:

$$\% \ CaCO_3 = \frac{B(f-ge)100}{G}$$

## RESULTS

The method is tried out by repeated titrations of three cement raw mixtures (A, B, and C), repeated by the same laboratory assistant and by different ones, as shown in Table 3, where the titration results — both within and between laboratory assistants — shows the extremely good reproducibility of the method.

The prerequisite of this good reproducibility in these examples is that the temperature and time for drying the samples are exactly the same in all analyses, as the samples may contain water of crystallisation and hydration, in addition to ordinary moisture, and thus may be difficult, if not impossible, to dry to constant weight in a reasonable time.

## Theoretical accuracy of the method

The content of $CaCO_3$ is calculated from the following formula: (see above)

$$\% \ CaCO_3 = \frac{B(f-ge)100}{G}$$

where $B$ and $e$ are again calculated from the formulae of the standardisations:

$$B = \frac{A}{a-be} \text{ and } e = \frac{c}{d}$$

*Table 3.* Titrations carried out repeatedly by the same laboratory assistant, and by different laboratory assistants.

| | | | |
|---|---|---|---|
| Raw material A | % $CaCO_3$ | | % $CaCO_3$ |
| | 77.33 | repeated by the same | 77.42 |
| | 77.47 | laboratory assistant 1 1/2 | 77.42 |
| | 77.40 | months later | 77.50 |
| | 77.38 | | 77.41 |
| | 77.40 | | 77.48 |
| | 77.39 | | 77.49 |
| | 77.37 | | 77.38 |
| Mean value | $\bar{a} = 77.39$ | | $\bar{a} = 77.44$ |
| Std. dev. on the individual determination | $s_a = 0.04$ | | $s_a = 0.05$ |
| Std. dev. on mean value | $s_{\bar{a}} = 0.02$ | | $s_{\bar{a}} = 0.02$ |
| Raw material B | 78.56 | repeated by another | 78.56 |
| | 78.55 | laboratory assistant 1 1/2 | 78.58 |
| | 78.56 | months later | 78.54 |
| | 78.57 | | 78.51 |
| | 78.52 | | 78.53 |
| | 78.57 | | 78.60 |
| | 78.69 | | |
| | $\bar{a} = 78.57$ | | $\bar{a} = 78.55$ |
| | $s_a = 0.05$ | | $s_a = 0.03$ |
| | $s_{\bar{a}} = 0.02$ | | $s_{\bar{a}} = 0.01$ |
| Raw material C | 78.56 | | 78.66 |
| | 78.64 | | 78.67 |
| | 78.60 | | 78.62 |
| | 78.54 | | 78.54 |
| | 78.58 | | 78.45 |
| | 78.54 | | 78.61 |
| | $\bar{a} = 78.58$ | | $\bar{a} = 78.59$ |
| | $s_a = 0.04$ | | $s_a = 0.08$ |
| | $s_{\bar{a}} = 0.02$ | | $s_{\bar{a}} = 0.03$ |

Each of these quantities is attended with inaccuracy: $f$, $a$, $c$, $G$, and $A$ with weighing inaccuracies which are known, and $g$, $b$, and $e$ with inaccuracies which will depend on the size of the drops, so that $\Delta g = \Delta b = \Delta e = 1/2$ drop expressed in grammes (the weighing inaccuracy on this quantity being without consequence).

By applying the "Law of Accumulation" to the determination of the inaccuracy on a physical quantity which is composed of independently measured quantities, it is possible to calculate $\Delta e$, $\Delta B$, and finally $\Delta$ % $CaCO_3$, using the following numerical values for a sample containing 80 % $CaCO_3$:

| | |
|---|---|
| $c$ = 5 g HCl sol. | $\Delta c$ = 0.00005 (weighing inaccuracy) |
| $d$ = 10 g NaOH sol. | $\Delta d$ = 0.006 (drop size inaccuracy) |

This gives: $\Delta e = 0.0003$

| | |
|---|---|
| $A$ = 0.25 g $CaCO_3$ | $\Delta A$ = 0.00002 g (weighing inaccuracy) |
| $a$ = 15 g HCl sol. | $\Delta a$ = 0.00005 g (weighing inaccuracy) |

| | |
|---|---|
| $b = 10$ g NaOH sol. | $\Delta b = 0.006$ g (drop size inaccuracy) |
| $e = 0.5$ g HCl sol. per 1 g NaOH sol. | $\Delta e = 0.0003$ (calculated) |

This gives: $\Delta B = 0.00001$

| | |
|---|---|
| $B = 0.025$ g $CaCO_3$ per 1 g HCl sol. | $\Delta B = 0.00001$ (calculated) |
| $f = 12$ g HCl sol. | $\Delta f = 0.00005$ g (weighing inaccuracy) |
| $g = 8$ g NaOH sol. | $\Delta g = 0.006$ (drop size inaccuracy) |
| $G = 0.25$ g of sample | $\Delta G = 0.00002$ g (weighing inaccuracy) |

This gives: $\Delta$ (% $CaCO_3$) = 0.05
The theoretical standard deviation of the method is thus:

$$s(\%\ CaCO_3) = 0.05$$

## CONCLUSION

The use of polyethylene spray bottles as weighing burettes provides a quick and accurate method of titration, where, with skilled laboratory assistant, the accuracy is of the same order of magnitude as the theoretical accuracy, as long as the spray bottle is handled with dry, clean hands.

The titration results show the extremely good reproducibility and accuracy of the method.

Incidentally, the method has a great advantage in the very simple equipment it calls for.

## REFERENCES

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