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Notes on Determination of Carbonates in Soils by Chemical Means, D. T. A., and X-Ray¹

By R. L. HANDY and TURGUT DEMIREL

Abstract. Various methods for measurement of carbonates in soils were tried and studied. Gas evolution methods are accurate but slow and susceptible to experimental error. Acid neutralization is rapid and offers a fair approximation, but it is affected by many non-carbonate minerals. Versenate methods are rapid and accurate, but are affected by exchangeable calcium on the clay. None of these methods is ordinarily specific for calcite or dolomite.

Differential thermal analysis is accurate and specific for calcite or dolomite. Best results were obtained by measuring peak height after runs in an air atmosphere. However, analyses are slow and are influenced by changes in the apparatus.

X-ray diffraction from a copper tube is accurate if peak area rather than peak height is measured, but the intensities are sensitive to the presence of iron, which absorbs most of the X rays. X-ray fluorescence measurement of calcium K α radiation is accurate and less susceptible to variable absorption, but since this method is affected by non-carbonate calcium, correction by leaching and re-testing is suggested. This appears to be the method most worthy of further examination.

The content of carbonate minerals in soils and unconsolidated sediments is of interest not only because carbonates indicate ancient and modern weathering zones and regional variations in unweathered material (Lyon, *et al.*, 1954) but also because of the effects on soil properties. Only a trace of carbonates influences pH, identity of exchangeable cations, plasticity, and potential use of a soil. Also, carbonates are important in acid methods of engineering soil stabilization, for example with phosphoric acid (Benn, 1959) or lignins (Demirel, 1959), since carbonate minerals react with acidic stabilizers and either increase or ruin their effectiveness. A method for rapid, precise measurement of carbonates, especially in the low content range, is therefore of prime importance.

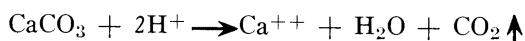
METHODS

Several methods for carbonate determination are used. The plan of this paper is to discuss these methods in general terms and point out their relative merits and disadvantages, and to present data on the search for a new method via differential thermal analysis, or X-ray fluorescent or diffraction techniques.

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Chemical Methods

Several methods for determining chemically the amounts of carbonates in soils are used. Unless accessory tests are used, however, these methods are non-specific for calcite, CaCO_3 ; dolomite, $\text{CaMg}(\text{CO}_3)_2$; or any other soluble carbonate. Results are usually calculated and reported as percent CaCO_3 . The methods all utilize dissociation of carbonates by acid:



Chemical methods fall into three categories, depending on whether they measure the number of hydrogen ions used up (acid neutralization), the amount of CO_2 gas evolved, or the number of calcium ions released in solution.

Gas evolution. Theoretically the most accurate methods for carbonate measurement involve treatment of a soil with excess hydrochloric acid and measurement of the CO_2 gas evolved. In fact, field identifications are usually made on this basis, the presence of 0.5 percent or more carbonate being indicated by the sight or sound of fizzing (USDA, 1954). In the laboratory the amount of gas evolved is measured volumetrically with a gas burette, or gravimetrically, for example by bubbling the CO_2 over soda-lime ($\text{NaOH} + \text{CaO}$) (Grant, 1944), or by weight loss in the sample (USDA, 1954).

For greatest accuracy these methods are slow and exacting, since they are susceptible to experimental error. Volumetric measurement of the gas requires correction for temperature and barometric pressure. In gravimetric measurement all HCl and water vapors must be trapped, and precise weighing is necessary to detect minute changes due to CO_2 . The reaction and evolution of gas from soils often requires 24 hours. Finally there is the problem of air initially dissolved in the acid and adsorbed on the soil mineral surfaces, and CO_2 dissolved and adsorbed after the reaction takes place. These can contribute to the error, e.g., samples 21-2 and 32-1, Table 1. Air is eliminated from the measurement by methods employing selective absorption. Error from dissolved CO_2 may be reduced by heating (Grant, p. 89).

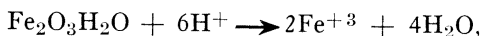
Acid neutralization. Measurement of CO_2 gas evolved is at best slow but sure, and is not well adapted to routine analysis. A far more rapid but theoretically less exact method is by acid neutralization, which means treating soil with an excess of hydrochloric acid and back-titrating to determine how much acid is used up (USDA, 1954). This method is perhaps the most widely used at present in soils work.

The major weakness of the acid neutralization method is the assumption that all acid is used by carbonates. Other minerals, such

Table 1
Carbonate Contents of Loess and Loessial Soils

Sample No.	Per cent 2μ		Per cent CaCO_3 by indicated method				
	clay	pH	CO_2	HCl	Versenate	DTA peak ht.	X-ray Fluor.
<i>Calcareous samples</i>							
16-1			11.56	12.00			
16-2			4.86	3.90			
18-1			11.39	13.62			
21-2			13.56	6.55			
33-1			13.62	11.50			
55-1	10.0	8.0	11.0		7.57		
49-2				16.2		10.4	11.4 \pm 0.5
22-1				15.0		9.4	11.5 \pm 0.6
23-1				12.3		7.7	9.3
24-1				11.8		7.4	9.0 \pm 0.7
<i>Leached samples</i>							
26-1	21.5	7.0		1.37			
30-1	29.5	6.4		1.62			
32-1			9.75	1.00			
36-1	28.9	6.6		1.75	0.73		1.6 \pm 0.4
46-1				1.50	0.89		
100-1					2.8		2.4 \pm 0.3
100-2					2.3		1.6 \pm 0.4
119-5		5.7			1.8		0.9 \pm 0.5
502-2	42.0	5.2			0.44		0.9 \pm 0.5

as gypsum, hydrous iron oxides, and clay minerals, are soluble or partly soluble in HCl. For example, dissolution of the hydrous iron oxide minerals goethite or lepidocrocite will mean



which uses up acid. A soil containing 2.0 percent by weight acid-soluble iron hydroxide and no carbonate will thus be erroneously reported as having 3.4 percent CaCO_3 .

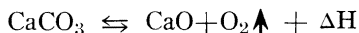
Versenate. To overcome some of the errors inherent in techniques in involving measurement of acid neutralization, versenate solutions may be employed specifically to measure Ca^{++} and Mg^{++} in the acid leachate. Versenate methods are rapid, and results are reproducible (Diehl and Smith, 1955). Unfortunately several sources of error remain. The presence of soluble noncarbonate Ca^{++} and Mg^{++} contributes error; in soils the most important source of this error is the exchangeable calcium held by the clay. Soils described in the field as leached (lower part of Table 1), and with a naturally acid pH, which automatically negates the possibility for carbonates, may show one-half to two or more percent carbonate by the versenate method. Acid neutralization similarly erroneously shows about 1.5 percent carbonate. A correction may be applied to versenate results if the cation exchange capacity and identity of the exchangeable cations are known,² but the validity remains questionable due to the different conditions in which the exchange takes place. Also these measurements require much more testing.

Calcite vs. dolomite. As previously mentioned, the usual techniques for carbonate measurement in soils do not involve separation of calcium and calcium-magnesium carbonates, and results are reported as percent CaCO_3 . Thus the presence of 5.0 percent dolomite, $\text{CaMg}(\text{CO}_3)_2$, will be reported as 5.5 percent CaCO_3 .

DIFFERENTIAL THERMAL ANALYSIS

Apparatus and Method

DTA is used for qualitative identification of clay minerals and carbonates in soils, and is recognized as a tool for qualitative analysis. In this method a sample is heated at a constant rate and differences in temperature between the sample and a sample of inert material heated in an identical manner are measured continually. The method is applicable to carbonates because of the calcination reaction.



²For example, a typical loess sample with 25 percent 2 micron clay will have a cation exchange capacity of about 20 m.e. per 100 gm. (Davidson and Handy, 1954), and nearly all exchange sites accompanied by calcium. This much exchangeable calcium will give a versenate-determined carbonate content of 1.0 percent.

ΔH is negative and ordinarily contributes an endothermic reaction peak at 700-900°C (Figure 1). Dolomite contributes two peaks, the first signifying breakdown of $MgCO_3$. Work in the present paper was limited to studies with calcite.

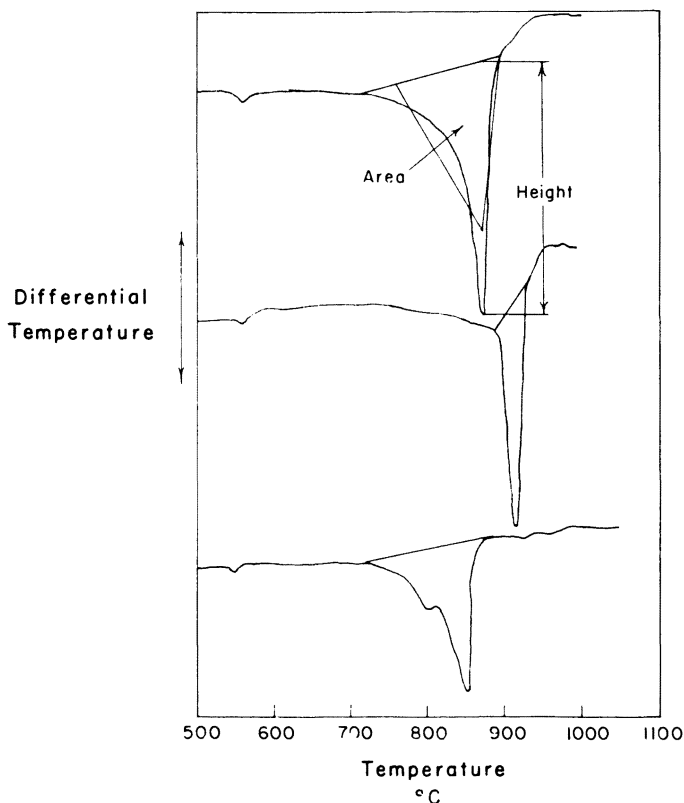


Figure 1. Typical DTA curves for calcareous soils. Labels on the upper curve show methods for measuring peak height and area. Middle curve was run with a CO_2 atmosphere, which delays the carbonate reaction. Lower curve shows the presence of dolomite.

The apparatus consists of vertical furnaces hung from the ceiling and counterbalanced for ease in lifting. An automatic heating rate controller provides for a rate of $10^\circ C$ per minute. The sample block of 18-8 stainless steel lies flat and is $\frac{3}{4}$ in. high by $1\frac{3}{4}$ in. in diameter. Two vertical $\frac{3}{8}$ in. d. by $\frac{1}{2}$ in. deep sample holes are symmetrically located with centers 1 in. apart. No. 22 Pt-Pt 10 percent Rh thermocouples are used. The furnace temperature couple is a separate chromel-alumel junction inserted in a $\frac{3}{8}$ in. d. by $\frac{1}{2}$ in. deep hole drilled up into the bottom of the block. The block is supported by a hollow ceramic pedestal.

Reactions

Factors affecting the size and shape of a DTA peak include the rate of heating (Smothers, 1958; Stone, 1951). More rapid heating gives sharper peaks and may affect peak area. This factor is therefore controlled.

Secondly, the DTA peak is affected by the rate of reaction, i.e., reaction kinetics (Murray and White, 1949, 1955). These are not readily mathematically predictable, but for one soil type they should be systematic so that if percent reactant is plotted against peak height or area, a smooth curve, but not necessarily a straight line, will result.

Thirdly, the peak will be affected by heat balance in the specimen, which depends on thermal conductivities and specific heats within the sample (Speil, 1945; Stone, 1951), and the composition of the atmosphere. Conductivities and specific heats are affected by simple particle size and packing, and will change during the reactions. Thus these variables defy mathematical treatment, but since they are systematic they should give smooth empirical relationships. Composition of the atmosphere should not affect simple transition reactions, for example the quartz inversion at 573°C, but it strongly influences the carbonate reaction. If thermal conductivity, specific heat, and influence of atmosphere and reaction rate all could be held constant, linear relationships between peak area and concentration of reactant would be expected (Speil, 1945).

Experimental Procedures

Artificial mixes. Since DTA peak parameters are expected to have systematic relationships with concentration of reactants, other factors being held constant, a friable calcareous loess soil from Harrison County, Iowa (Sample 20-2VII) was leached with HCl, re-enriched with different amounts of C.P. calcium carbonate, and run by DTA. Thermocouple junctions previously had been accurately centered in the sample holes, and a uniform hand packing procedure was adopted. Analyses were run in air and in CO₂ at one atmosphere.

Typical DTA curves on these mixtures are shown in Figure 1. Peak heights and areas were measured as shown. These are plotted against percentage carbonate in Figure 2.

First it will be noted that in air the reactions begin at about 700°C and reach a peak at a temperature related to carbonate content. See Figure 2 (a). Thermal lag within the sample caused by heat used by the reaction is insufficient to explain this gradual peak displacement, which reaches a maximum of 90°C. This suggests that CO₂ released from the reaction builds up a partial pressure and acts as a retarder. Since this in turn undoubtedly affects ΔH ,

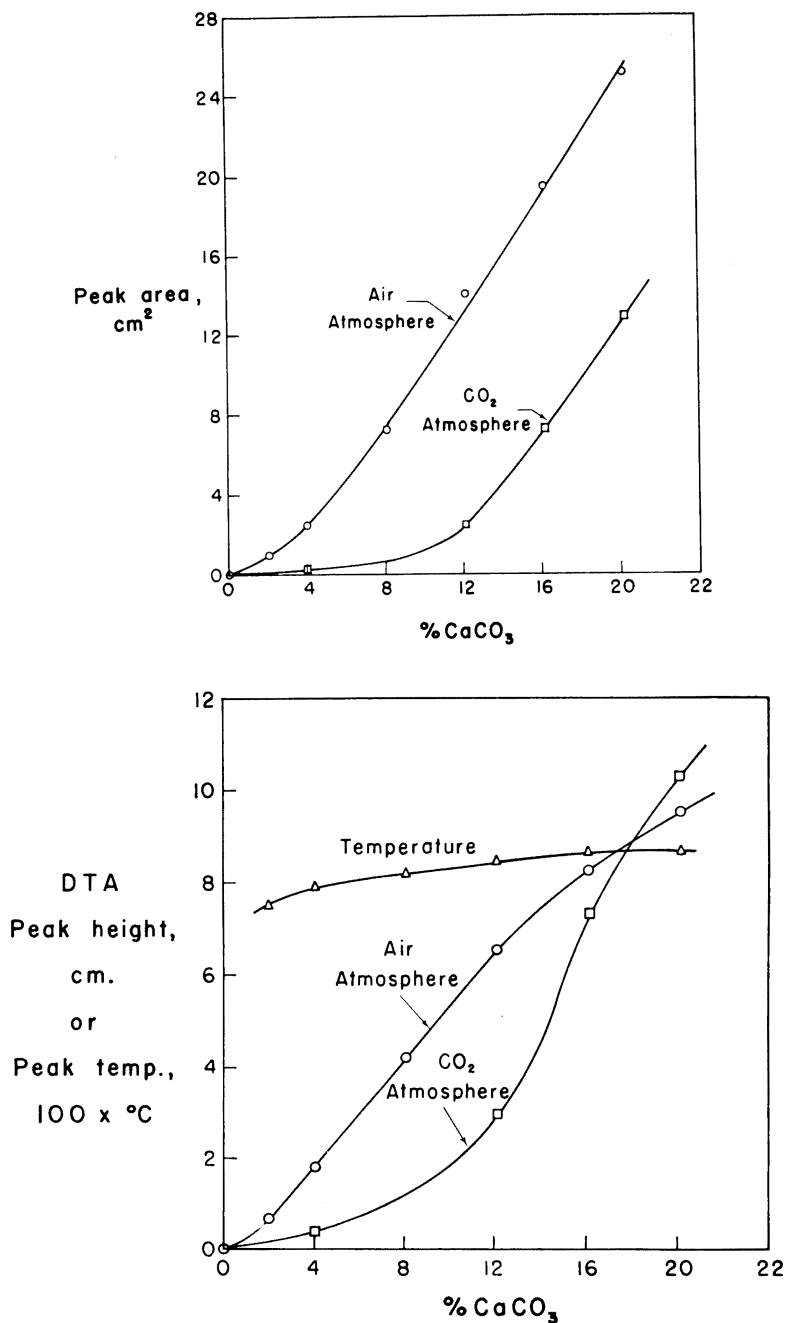


Figure 2. Top graph shows relationship between per cent calcite and DTA peak area from prepared samples. Lower graph shows per cent calcite vs. peak height for an air atmosphere and for a CO₂ atmosphere, and shows the shift in peak temperature for runs in air.

quantitative relationships are not expected to be linear. Figure 3 verifies this.

It was therefore decided to try to control the atmosphere by introducing CO₂, a decision also reached by many other researchers. In a CO₂ atmosphere the decomposition reaction does not begin until the temperature is about 830°C. As seen in Figures 1 and 2, peak height and area are greatly reduced, a further indication that ΔH varies considerably depending on reaction temperature and environment. At high carbonate contents the plotted relationships for runs in air and in CO₂ more closely match, further suggesting that CO₂ pressure becomes significant even when the only source for CO₂ is the reaction itself.

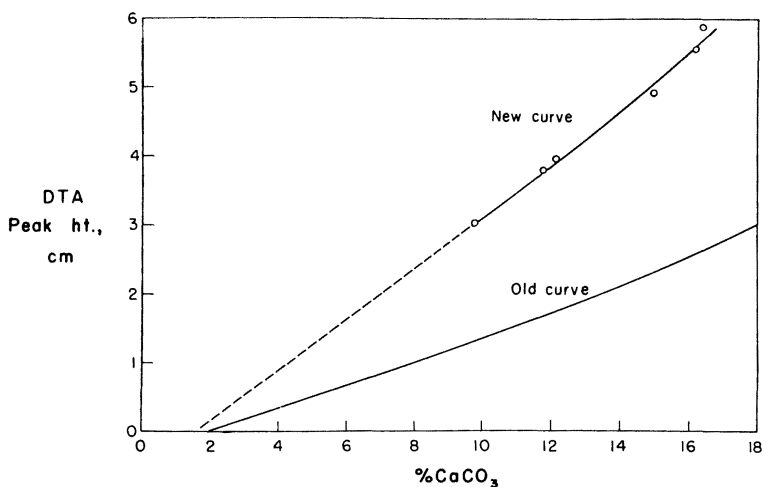


Figure 3. DTA calcium carbonate calibrations for natural soils. New curve resulted from from a thermocouple re-alignment.

The CO₂ atmosphere in general decreases the linearity of plotted relationships, particularly in the low carbonate content range. Several possibilities may be suggested—perhaps the CO₂ did not permeate the sample adequately, or perhaps small differences in temperature are muffled by heat transfer from the flowing gas. Rather than attempt to use gas pressure techniques, use of CO₂ was discontinued.

Natural soils. Non-linearity and lack of a precise mathematical relationship for the plotted curves prevent use of equations with added amounts of carbonates as internal standards, as in X-ray fluorescence analysis, discussed below. The only method remaining is preparation of empirical calibration curves. For the curves in Figure 2, the noncarbonate matrix was a single loess soil; it was

next decided to see if the same curve might hold when the matrix varies.

A plot of peak height vs. carbonate content of different natural loess samples gives a curve with a different slope, Figure 3. However, the reference carbonate measurements, made by acid neutralization, are very questionable. DTA carbonate percentages using the curve in Figure 2 (a) are reported in Table 1 and agree well with X-ray analysis.

It also may be shown that DTA peak height is particularly sensitive to thermocouple alignment. An older calibration curve, also in Figure 3, gives even a different slope.

In conclusion, it is suggested that the DTA method may be used as an accurate means for carbonate determination if careful calibration tests are performed for each different type of soil. Figure 2 (a) may be regarded as a tentative calibration curve for loess soils. The next phase of work would be to study further the effect of matrix, and to investigate the reactions with dolomite (Haul and Heystek, 1952).

X-RAY METHODS

Carbonates are determined by two methods of X-ray analysis. In one the sample is subjected to hard, short wavelength X-rays and secondary fluorescence is measured (Handy and Rosauer, 1959). This method will measure total calcium and/or magnesium, but is not specific for carbonates. The second method is by X-ray diffraction and measurement of the intensity of the diffraction peaks. This method will be specific for calcite, dolomite, or other carbonate minerals. Both methods may be rapid, since no weighing or pre-treatment is required.

Because of the drawbacks in chemical tests and DTA, a preliminary investigation was made to determine if one of the X-ray methods might be more accurate and practical. The first problem was to ascertain sensitivity and linearity of relationships. For this purpose the artificially prepared reference soils were used.

X-RAY FLUORESCENCE

Soil samples bombarded with hard X-rays fluoresce, or give off their own radiation with wavelengths and intensities characteristic of elements in the sample. To test for calcium, $\text{CaK}\alpha$ radiation is isolated for intensity measurement by diffraction at the Bragg 2θ angle from an EDDT crystal. The fluorescent radiation was counted with a gas flow counter tube. Each N value reported is the average of ten counts of ten seconds each. Use of an automatic calculating machine in conjunction with the counting allows computation of

variance and 95 percent confidence intervals while the counts are being made (ASTM, 1957).

Samples were pulverized and packed dry into sample holders, and background counts were made on each sample at an angle of 2θ less 1° . Background counts were subtracted from the counts for $\text{CaK}\alpha$. A reference standard sample of powdered C. P. calcium carbonate was found to give an average $\text{CaK}\alpha$ count of 17,360 cps; if in future work the count on this reference changes, results may be adjusted by multiplying by a proportionality factor.

The excellent linearity and low scattering of points in Figure 4 suggests that X-ray fluorescence is an accurate method for carbonate determination. Also it is very rapid, requiring about five to ten minutes per sample, including corrections for background and calculations for variance.

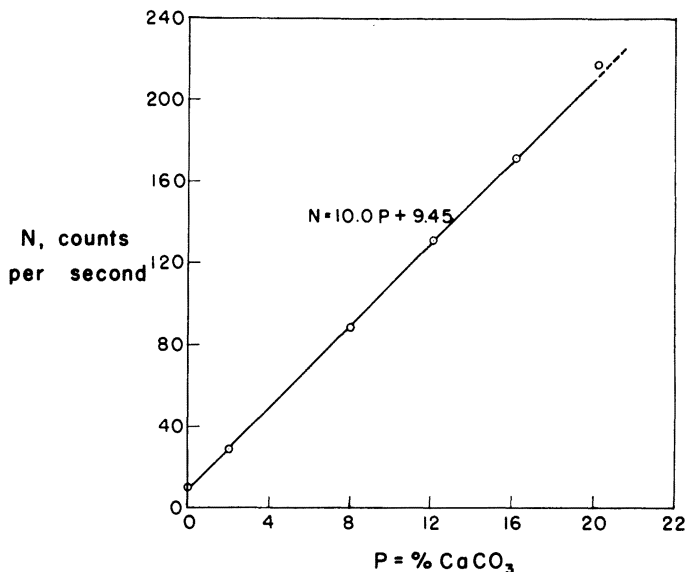


Figure 4. X-ray fluorescent calibration curve for calcium carbonate. Since X-ray fluorescence measures total calcium, some counts result from samples with zero per cent carbonate.

The major influence of matrix is to reabsorb fluorescent X-rays before they leave the sample, the amount of absorption depending on the other elements present. Therefore, elements having high absorption coefficients will reduce X-ray intensities. Fortunately most of the common elements in soils have approximately the same absorption coefficients for $\text{CaK}\alpha$ radiation (Table 2). Chlorine, sulfur, and phosphorus are the critical elements with very high absorption coefficients, but these are not common in soils. Therefore the influence of changes in matrix may be small so long as the differences

are within reasonable limits. The calibration curve of Figure 4 probably applies therefore to a wide variety of Midwestern loess and glacial soils.

Table 2

Mass Absorption Coefficients of Different Elements for CaK α and CuK α Radiations

Element	Atomic number	μ/ρ	
		CaK α ¹ $\lambda = 3.36 \text{ \AA}$	CaK α ² $\lambda = 1.5418 \text{ \AA}$
C	6	43	4.9
Al	13	417	48.5
Si	14	520 ³	60.3
P	15	610 ³	73.0
S	16	780	91.3
Cl	17	870	103.4
K	19	~ 200 ³	143
Ca	20	~ 200 ³	172
Mn	25	280 ³	284
Fe	26	312	324

¹Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., 35th Ed., 1953.

²International Tabellen zur Bestimmung von Kristallstrukturen, Vol. 2, 1935.

³Interpolated on basis of atomic number.

Another problem, that of calcium not occurring as carbonate, is indicated by the count of 9.45 on the reference soil with zero percent carbonate (Figure 4). To see if this count differs in different soils, several leached loess soils having zero percent carbonate were tested. Unfortunately the zero count was found to vary from 9.1 to 23.5 in different samples. (Calculated percentages for these samples are in the lower right of Table 1.) Therefore the best method for correction may be to leach each sample with HCl, count for non-carbonate calcium, and subtract this from the result for the untreated soil.

Fluorescent analyses uncorrected for non-carbonate calcium and utilizing the relationship in Figure 4 ($P = N/10$) are presented in Table 1. If the average correction is taken as 1.5 percent and subtracted from fluorescent percentages, the results will be close to those from DTA. The most accurate procedure, however, would be to determine corrections for each sample by leaching and re-running.

X-RAY DIFFRACTION

X-ray diffraction is a precise method for carbonate analysis, since it is specific for each crystal structure. In this study filtered copper K α radiation was used. Two counting methods were employed to measure the intensity of the diffraction: (a) The peak height above background was obtained by first scanning with both increasing and decreasing 2θ angles to locate accurately the center of the peak, and the height was measured at the center of the peak by manual counting for 10 ten-second counts. Usually the 2θ angle was in the neighborhood of 29.2° , and background counts were made at a 2θ

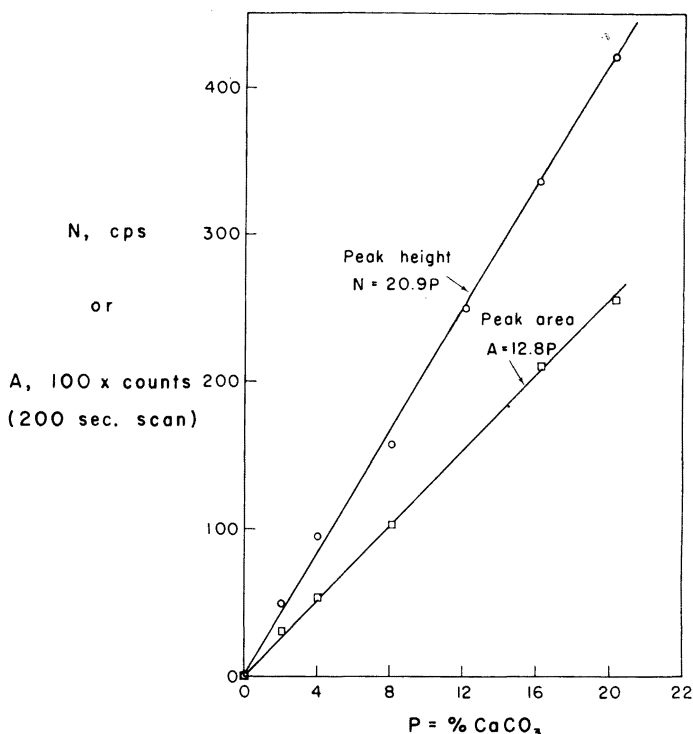


Figure 5. X-ray diffraction calibration curves for calcite. Curves were fitted by least squares.

of 29.0°. (b) The peak area was obtained by slow scanning (0.2° per minute) across the peak, usually 29.0° to 29.667°; recording total counts; and then subtracting counts for 29.0° background.

Results on artificially mixed soils, Figure 5, indicate good linear response with no erroneous carbonate reported for the leached sample. The scatter of points may be partly attributed to high background, but known percentages of carbonate of three out of the seven reference samples fall outside of the 95 percent confidence limits from counting (Table 3), suggesting appreciable sample error.

Scatter of points is less with the area counting method; the average error in seven determinations is 0.15 percent carbonate as against an average of 0.26 percent by the peak height method. The sample error appears to be reduced by scanning a diffraction peak rather than counting for maximum height. This suggests that the sample error may be from imperfectly random grain orientation, an effect much diminished by scanning. The scanning method is also the more rapid method for routine analysis.

As in the fluorescent analysis, the next question is absorption of X-rays by the samples, particularly when samples vary. As seen in Table 2, absorption of diffracted $\text{CuK}\alpha$ X-rays can vary considerably depending on the element in the sample, the worst sponge being iron.

Table 3
Carbonate Contents By X-ray Diffraction Peak Height Method

Sample	Per cent CaCO_3	Counts per sec. ¹			Per cent CaCO_3 from graph
		Peak	Background	N	
<i>References mixes</i>					
R 0	0.00	118.8 ± 3.2	118.9 ± 1.8	0 ± 5.0	0 ± 0.25
R 83	2.03	165.6 ± 3.2	115.8 ± 2.5	49.8 ± 2.5	2.38 ± 0.27
R 35	4.05	215.7 ± 3.1	120.5 ± 3.2	95.2 ± 6.3	4.55 ± 0.30
R 65	8.10	278.5 ± 3.9	121.1 ± 2.6	157.4 ± 6.5	7.55 ± 0.31
R 1	12.15	362.6 ± 4.3	113.4 ± 2.9	249.2 ± 7.2	11.9 ± 0.3
R 19	16.19	454.3 ± 5.0	118.1 ± 2.7	336.2 ± 7.7	16.1 ± 0.4
R 51	20.24	545.4 ± 5.4	122.5 ± 3.8	422.9 ± 9.2	20.2 ± 0.4
<i>Natural soils</i>					
49-2	7.57 ²	135.3 ± 3.1	108.8 ± 3.0	26.5 ± 6.1	1.27 ± 0.29
23-1	12.3 ²	142.7 ± 3.2	112.2 ± 3.0	30.5 ± 6.2	1.46 ± 0.30
100-1	2.8 ²	138.0 ± 4.4	128.6 ± 2.3	9.4 ± 6.7	0.45 ± 0.32

¹The ± entry indicates 95 per cent confidence limits (0.754 times the standard deviation) for each value which is the average of 10 determinations.

²Versenate method for total acid-soluble Ca^{++} and Mg^{++} .

Several loess samples were tested by X-ray diffraction (Tables 3 and 4). Intensities were far below those from prepared samples, probably because acid leaching of the prepared mixes removed much of the iron. The count-scan method gave higher percentage than peak counting, indicating diffraction line broadening due either to poor crystallinity or fine crystallite size of the carbonate. The scan method appears to be the best one, but quantitative diffraction work will require use of internal standards or a different target X-ray tube.

Table 4
Carbonate Contents By X-ray Diffraction Peak Area Method

Sample	Per cent CaCO_3	Total counts ¹			Per cent CaCO_3 from graph
		Peak	Background	A	
<i>Reference mixes</i>					
R 0	0.00	24,000	23,780	220	0.17
R 83	2.03	24,910	21,900	3,010	2.35
R 35	4.05	29,450	24,100	5,350	4.14
R 65	8.10	34,520	24,220	10,300	8.05
R 1	12.15	38,240	22,680	15,560	12.2
R 19	16.19	44,910	23,620	21,290	16.6
R 51	20.24	50,430	24,500	25,930	20.2
<i>Natural soils</i>					
49-2	7.57 ²	25,150	22,230	2,920	2.28
		24,730	21,740	2,990	2.34
		24,210	21,250	2,960	2.31
23-1	12.3 ²	28,640	22,450	6,190	4.83
100-1	2.8 ²	25,770	24,660	1,110	0.866

¹Peak scanned at $0.2^\circ 2\theta$ per minute from $2\theta = 29.0^\circ$ to 29.667° Background counted at $2\theta = 29.0^\circ$.

²Versenate method for total acid soluble Ca^{++} and Mg^{++} .

CONCLUSIONS

1. Carbon dioxide evolution methods are accurate but slow, and great care is required in the analysis. Errors result from adsorbed and dissolved gases.
2. Measurement of carbonates by acid neutralization is rapid but it is only approximate due to other minerals which may react. In loess soils the error is commonly plus one or two percent carbonate, regardless of whether samples are calcareous or leached.
3. Versenate solutions may be used to distinguish calcium and magnesium ions in the acid leachate, but results are in error because of exchangeable calcium held on the clay. With loess the error is commonly plus 1 to 2.5 percent carbonate, regardless of whether samples are calcareous or leached.
4. Less serious error is introduced by reporting dolomite as calcite.
5. Differential thermal analysis is specific for calcite or dolomite. For best quantitative results DTA peak height is measured, the atmosphere during the run being air. DTA unfortunately is quite sensitive to changes in furnace and thermocouple alignment. One run requires about 1½ hours. Equipment maintenance costs are high.
6. Since X-ray fluorescence measures total calcium in a sample, the results are similar to those from versenate testing, except that magnesium is measured separately if at all. The X-ray method requires about five to ten minutes per sample compared with about one hour for versenate testing, and trace amounts of calcium may be detected. Correction for non-carbonate calcium may be made by acid leaching and re-testing. Absorption is not expected to vary appreciably in common Iowa soils, but can be corrected for by use of internal standards. Of the various test methods investigated, X-ray fluorescence appears most worthy of future investigation and use.
7. X-ray diffraction with $\text{CuK}\alpha$ radiation is accurate but overly sensitive to presence of iron, which absorbs the $\text{CuK}\alpha$ X-rays. Best results are obtained by count-scanning the diffraction peak and making allowances for background. Better results could be obtained with use of a different tube.

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