AUTOMISED POTENTIOMETRIC END POINT TITRATION FOR CARBON AND ORGANIC MATTER DETERMINATIONS

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Intisari

Pengukuran bahan organik tanah dengan metode ''Dichromate Wet Combustion'' meliputi proses titrasi senyawa dikhromat yang tersisa dengan menggunakan ion ferro. Titrasi redoks potensiometrik diduga mampu berperan sebagai pengganti metode indikator warna diphenilamina. Modifikasi ini memungkinkan pengukuran akhir yang cepat dan teliti, dan dapat diandalkan bagi laboratoria yang analisis rutinnya mencakup pengukuran bahan organik. Metode usulan ini diperbandingkan dengan metode konvensional Walkley dan Black, untuk tanah-tanah mineral yang berbeda dari Jawa Barat dan Jawa Tengah, untuk gambut untuk kompos dan limbah organik. Metode usulan terbukti sangat teliti dan dapat diulang serta dapat direkomendasikan bagi pengukuran bahan organik tanah di laboratoria penguji tanah.

Abstract

The dichromate wet combustion determination of soil organic matter involves a titration of the excess of dichromate with ferrous ions. An automised potentiometric redox titration is proposed as a substitute for the diphenylamine colour indicator method. This modification enables a fast and accurate end point determination, and is very reliable for laboratories where organic matter determinations are part of the routine analysis. The proposed method is compared with the traditional Walkley and Black method for different mineral soils from West and Central Java, for peat, for compost and organic waste. The proposed method is highly accurate and reproducible and can be strongly recommended for soil organic matter determinations in soil testing laboratories.

I. Introduction

The term *soil organic matter* embraces the whole non-mineral fraction of soil and any vegetable or animal matter forming part of the sample analysed, will be included in the determination. Thus analytical results depend in the first place upon the size of the sieve used in the preparation of the sample (*Hesse, 1971*).

Soil organic matter has a structure which is too complex to be determined as such, but its composition is remarkably constant. Carbon is the main building-block of soil organic matter, comprising from 48% to 58% of the total weight (*Nelson and Summers, 1982*).

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Therefore, total organic matter is estimated on a routine basis from the determination of oxidizable carbon in the soil sample.

The principle of total carbon analysis is to convert the element completely into carbon dioxide which is then determined gravimetrically or volumetrically Oxidation is achieved by either wet or dry combustion.

The quantitative determination of soil organic matter by the dichromate-wet combustion method (*Nelson and Summers, 1982*) is a commonly used procedure, especially for routine analysis in soil testing laboratories. The method is based on the oxidation of organic carbon by dichromate in acid medium and is well-known as the Walkley and Black procedure (*Walkley and Black, 1934*). The main disadvantage of the method is that the oxidation of organic carbon is incomplete and this necessitates the use of a correction factor, which means that the results obtained cannot be considered as quantitative. The main advantage of the procedure is its simplicity and rapidity.

The excess dichromate is back-titrated with a standard ferrous reducing solution. The main difficulty in the titration is the detection of the end point. Several minor modifications of the method exist, using different end point colour indicators: diphenylamine in phosphoric acid medium (*Schollenberger, 1945*), barium diphenylamine sulphonate (*Peech et al., 1947*), ortho-phenantroline (*Jackson, 1958*), N-phenylanthranilic acid (*Simakov, 1957; Mebius, 1960*).

However, instead of relying entirely upon a colour change, the excess dichromate can be titrated potentiometrically (*Raveh and Avnimelech, 1973*), in which case no indicator is required.

The objective of this paper is to describe a potentiometric method, using an automatic titration system. The proposed method is based on the use of redox potential measurements for the determination of the end point in the titration. A comparative study is done for the diphenylamine and the automised potentiometric titration, using mineral soils from West and Central Java, peat, compost and organic waste materials. Saccharose ($C_{12}H_{22}O_{11}$), is used to check accuracy and precision.

II. Background and Theory

The oxidation of organic C by dichromate in acidic medium proceeds according to the following reactions:

$$4\,(Cr^{6+} + 3\,e \rightarrow Cr^{3+})$$
$$\underline{3\,(C - 4\,e \rightarrow C^{4+})}$$
$$4\,Cr^{6+} + 3\,C \rightarrow 4\,Cr^{3+} + 3C^{4+}$$

In the Walkley & Black method the reaction is as such:

$$2\,K_2Cr_2O_7 + 3\,C + 8\,H_2SO_4 \rightarrow 2\,K_2SO_4 + 2\,Cr_2(SO_4)_3 + 3\,CO_2 + 8\,H_2O \ldots\ldots \quad (1)$$

The soil sample is treated with an excess dichromate. After oxidation, the excess dichromate is back-titrated with a standard ferrous reducing solution, giving the reactions (acidic medium):

$$6\,(Fe^{2+} - e \rightarrow Fe^{3+})$$
$$\underline{2\,(Cr^{6+} + 3\,e \rightarrow Cr^{3+})}$$
$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^{+} \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O \,.. \quad (2)$$

Reaction (2) expressed in terms of redox potential (of the half cell relative to the normal hydrogen electrode) consists of two Nernst's equations:

$$E(V) = E^{\circ}_{Fe2+} - \frac{0.059}{1} \times \log \frac{[Fe^{2+}]}{(Fe^{3+}]} \ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$E(V) = E^{\circ}_{Cr_2O_7} - \frac{0.059}{6} \times \log \frac{[Cr^{3+}]^2}{[Cr_2O_7{}^{2-}] \times [H^{+}]^{14}} \ldots \quad (4)$$

where $E^{\circ}_{Fe2+} = 0.77$ V and $E^{\circ}_{Cr_2O_7} = 1.33$ V.

Table 1 describes the potentiometric titration in terms of redox-potential and concentration of the different ions involved in the reaction, under the experimental conditions of:

- — 10 ml $K_2Cr_2O_7$ 1N = 1.67×10^{-3} mol $Cr_2O_7^{2-}$ in 10 ml
- — 20 ml H_2SO_4 36N = 0.72 mol H^{+} in 20 ml
- — a total volume at the start of (10 + 20 + 150 =) 180 ml.

There is a marked voltage shift (drop) at the end point of this reaction in the order of 400 mV for 0.02 ml of titrant. The change in potential during the potentiometric titration of $Cr_2O_7^{2-}$ by Fe^{2+} is given in figure 1 for 3 replicates of the blank titration (10 ml K_2CrO_7 + 20 ml H_2SO_4 + 150 ml H_2O).

The difference between the experimental and the theoretical (calculated) value of E (V) can be explained by the potential difference between the reference Ag/AgCl-electrode used and the normal hydrogen electrode (199 mV, *Stumm & Morgan, 1981*) and by the use of concentrations in stead of activities. Besides this, sulfuric acid may reduce the formal potential of the $Cr_2O_7^{2-}/Cr^{3+}$ couple, as hydrochloric and phosphoric acid do (*Christian, 1986*).

III. Materials and Methods

3.1. Materials

We collected different material available at the Soil Science Department of the Faculty of Agriculture, University of Gadjah Mada, Yogyakarta. The origin, type and certain characteristics are shown in table 2a and 2b. All dried samples passed through a 2 mm sieve for the chemical characterisation and through an 0.5 mm sieve for the carbon determinations. Moisture content is given on air dry basis, pH was measured using a 1: 2.5 (w/v) soil/solution ratio. The exchangeable cations were extracted with 1N NH_4OA_c (pH 7) and determined by flamephotometry.

3.2. Procedure

Automatic titration for mineral soils

Exactly 1 g of soil is weighed into a 250 ml conical flask (with wide mouth), 10 ml of 1N $K_2Cr_2O_7$, is added and immediately afterwards 20 ml concentrated H_2SO_4 (36N). Soil and solution are mixed gently, and digested for 30 minutes in the fumehood.

The automatic titration system is made ready. The system used consists of the Radiometer TTT85 Titrator and ABU80 Autoburette, and has been programmed for the organic matter determinations. The settings of the programme are given in table 3.

The titration is made with a Pt-electrode as indicating electrode and a Ag/AgCl-electrode as reference. The off-set value should indicate zero. The end point method is selected on the Titrator TTT85 and the speed selector on the Autoburette ABU80 should be set to the value of 20 and the volume selector at 1/10. The titrant reservoir is filled with 1N Fe $(NH_4)_2(SO_4)_2.6H_2O$ (Mohr's salt) solution. A complete rinsing of the system and the expulsion of all air bubbles is done with the flush programme on the Autoburette. The flush programme is completed in = 5 minutes and leaves the Autoburette filled and ready for use. After reacting the digest for 30 minutes, 150 ml demineralised water is added and the electrodes are dipped into the suspension, which is stirred gently using a magnetic stirrer.

The mV reading on the titrator will indicate a value between 1000 and 1050 mV. After dipping the glass delivery tip into the suspension, the automatic titration is started. The Autoburette will automatically switch off when the Titrator detects the sharp potential drop around 800 mV (see table 1). After reaching the end point the reading in ml indicated by the Titrator corrects for eventual overshooting.

The flask can be replaced with another sample, and the next titration can start. A blank titration containing only dichromate should be treated exactly in the same way as the samples, in order to standardise the ferrous solution against the dichromate.

Calculations

If "A" ml ferrous solution is added to the blank and "B" ml to the sample, then the titration difference (A-B) ml will be equivalent to the amount of dichromate reduced by the organic C in the sample. According to the stoichiometry of the redox reaction (1), 10 ml 1N $K_2Cr_2O_7$ (or 10 meq $K_2Cr_2O_7$) has the potential to oxidize 10 meq C. Since the method assumes C to have a valence of 4 in most organic compounds, 10 meq C is equivalent to 30 mg C (this assumption is common in all wet combustion determinations, although no studies can be found to evaluate the assumption).

Since the normality of the ferrous solution is uncertain, it can only be established by standardisation against the 1N $K_2Cr_2O_7$ solution. However, it is not necessary to know the absolute normality of the ferrous solution. The relative proportion (between 0 and 1) of dichromate which has reacted with organic C in the soil is equal to (A-B)/A.

For 1 g of soil, the oxidizable organic C content (C_o) will then be: $C_o = 30 \times (A\text{-}B/A)$ mg or $\%C_o = 3 \times (A\text{-}B)/A$. Experience has shown that the oxidation with $K_2Cr_2O_7$ only yields about 75% of the total organic C present (*Dynoodt, 1991*). This is taken into account by setting the C-equivalent equal to 4 instead of 3. The total organic C content (C_t) is thus found as: $\%C_t = 4 \times (A\text{-}B)/A$.

Finally, assuming that soil organic matter (O.M) consists of 50% C, the total organic matter is derived as: $\%O.M. = 2 \times \%C_t$.

REMARK: It is evident that estimation of organic matter content from organic C concentrations is not highly accurate, because the ratio organic matter to organic C is variable from soil to soil and *with depth in the profile. Accurate organic matter content estimates require a knowledge of the factor for the particular soil studied. However, if an estimate of organic matter content of surface soils mush be made based on organic C data and no information on the exact factor is available, a factor of 2 appears to be most universally acceptable (Nelson and Summer, 1982).*

Organic materials

The samples are treated in a slightly different way for peat, compost, sludge and other organic material because of the higher organic C content: 0.1 or 0.5 g material is weighed and 20 ml of 1N $K_2Cr_2O_7$ solution is added. The amount of $K_2Cr_2O_7$ will influence the calculations of C_t with a factor 2 (20 meq $K_2Cr_2O_7$ oxidizes 20 meq C or 60 mg organic C).

Walkley and Black method

The organic C determinations with the procedure described above are compared with the results using the conventional Walkley and Black titrimetric determinations: 1 g of soil is weighed, 10 ml of 1N $K_2Cr_2O_7$ is added and immediately afterwards 20 ml concentrated H_2SO_4 (36N). Soil and solution are mixed gently and stored for 30 minutes. Then, 150 ml demineralised water is added and the suspension is filtered through a Whatman 42 filterpaper. Concentrated H_3PO_4 (10 ml) and 10 drops of diphenylamine indicator solution are added. The solution is titrated with a 1N solution of $Fe(NH_4)_2(SO_4)_2.6H_2O$, using a microburette.

Initially the solution will be yellowish brown. Progressively the colour will change over blue to violet, which is a sign that the equivalence point is near. Upon further slow addition of $Fe(NH_4)_2(SO_4)_2$-solution, the colour abruptly changes to green.

A blank titration, containing only dichromate, is carried out following the entire oxidation and titration procedure in order to standardise the $Fe(NH_4)_2(SO_4)_2$-solution.

IV. Results and Discussion

Accuracy and Precision

The carbon content of a sugar (saccharose) was determined in order to check the accuracy of both methods. The Molecular Weight of saccharose $C_{12}H_{22}O_{11}$ equals 342.30 g, thus 40 mg saccharose contains 16.827 mg C. Using the automised method the amount of C found was 16.820 mg, 16.788 mg, 16.784 mg respectively, or a recovery percentage (relative accuracy) of 99.96%, 99.77% and 99.74% (99.82% on average).

Using the diphenylamine method the amount of C found was 17.144 mg, 17.184 mg, 17.184 mg respectively, or a relative accuracy of 101.88%, 102.12% and 102.12% (102.12% on average).

It shows there is a slight overestimation when using the conventional Walkley and Black method. This may be due to the unexperience of the analyst, but it shows at least that the automatic titration is not influenced by this kind of problems and is thus more accurate and reliable.

During the carbon determinations of all the material listed in table 2a, ''compost'' (nr.21 in table 2a) was regularly repeated in the sequence of analysis in order to check more thoroughly the statistical meaning of the results obtained by both methods. The results given in table 4 show that the Standard Deviation is higher using the diphenylamine titrimetric determination. The Coefficient of Variation amounts 4.47% for the diphenylamine method and is 2.33% for the automatic redox titration. The precision of the latter is thus slightly better.

Organic Matter Determinations

The results of the organic matter (O.M.) determinations for different material listed in table 2a are shown in table 5. Comparing the results of both methods, one can conclude that:

(1) Nearly all values are slightly lower when using the proposed automised method. Based on the results of the recovery test, one can say there is an overestimation of the O.M. content when using the conventional Walkley & Black procedure. This overestimation is small and thus not of big concern, but it shows at least the higher reliability and accuracy of the automised method.

(2) The Standard Deviation for 3 replicates is usually higher when using the proposed automised method. Comparing this with the Standard Deviation for both methods in the recovery and accuracy tests with saccharose and compost, the lower Standard Deviation here (i.c. for 3 replicates in a row, in stead of 10 replicates at random through the whole experiment) can be explained by the prescience of the analyst. Again, this is not of big concern, but it favours the automised titration method once more: although giving higher Standard Deviations, the results are more reliable.

(3) The determined value of organic matter for peat is higher than 100% and this is of course not possible. It can be explained by the use of the factor 2 (common for mineral soils) in the calculations when converting % C_t to % O.M.

Based on the ash content only, the O.M. content of the organic materials (see table 2a) can be estimated as given in table 6. This results in conversion factors C_t/O.M. that differ from the 0.50 used. These factors are not of greater value than the others, any constant factor used remains an approximation at best.

More detailed experiments concerning the total carbon determinations in different organic soils using the proposed automised method, in combination with the determinations of ash content and degree of decomposition, are necessary to find out what conversion factor(s) could be more suitable for organic soils. The lower the degree of decomposition the lower the recovery. It is recommended to use the Mebius procedure (*Mebius, 1962*) with external heating.

VI. Conclusion

The potentiometric redox titration is highly accurate and precise, and is not giving overestimates as in the case of the titrimetric determinations.

The subjectivity and the prescience of the analyst is excluded using an automised method. The carbon determinations become thus more reliable.

Unexperienced analysts can confuse the dirty green colour at the beginning of a titration with the green colour of the end point, but this is merely due to lack of practice.

The lesser accuracy for the titrimetric determinations is compensated by the rapidity and simplicity of the method, but analysts confirm the much more pleasant determinations using the automatic titrator.

By using the automised procedure, the carbon determinations become less expensive in terms of chemicals and glassware.

Resuming all this one can strongly recommend the automised potentiometric end point titration for routine carbon determinations in soil testing laboratories.

Table 1. **Description of the potentiometric redox titration of $Cr_2O_7^{2-}$ by Fe^{2+}**

Titration Point	ml Fe^{2+} Added	Total Volume (ml)	$[Cr_2O_7^{2-}]$ (mol/l)	$[Cr^{3+}]$ (mol/l)	$[H^+]$ (mol/l)	E (V)
start	0	180	9.28×10^{-3}	0.00	4.00	—
1% neutralisation	0.1	180.1	9.18×10^{-3}	1.85×10^{-4}	4.00	1.466 [1]
10% neutralisation	1	181	8.30×10^{-3}	1.85×10^{-3}	3.98	1.445 [1]
90% neutralisation	9	189	8.84×10^{-4}	1.59×10^{-2}	3.81	1.415 [1]
equivalent point	10	190	0.00	1.76×10^{-2}	3.79	1.331 [2]
0.2% over equiv.pt.	10.02	190.02	0.00	1.76×10^{-2}	3.79	0.929 [3]
1% over equiv.pt.	10.1	190.1	0.00	1.76×10^{-2}	3.79	0.888 [3]

(1) : equation (4) is used.

(2) : equation (3) & (4) are used (at equivalent point, the concentrations are: $[Fe^{2+}] = 6 \times [Cr_2O_7^{2-}]$

(3) : equation (3) is used.

Table 2a. **Type and origin of the material used for C-determinations**

nr	Type of Material	Origin of Material
1	Vertic Rhodudalf	Mulo, Gunung Kidul, Central Java
2	Typic Rhodudalf	Jasinga, Bogor, West Java
3	Entic Pelludert	Gading, Gunung Kidul, Central Java
4	Entic Udipsamment	Kalitirto, Yogya, Central Java
5	Dystric Troposaprist	Pontianak, West Kalimantan
6	Eutric Troposaprist	Rawapening, Salatiga, Central Java
7	Rhodic Paleudalf	Ungaran, Semarang, Central Java
8	Typic Tropofluvent	Samas Beach, Central Java
9	Udand	Boyolali, Central Java
10	Compost sugarcane factory	Sugarcane factory, Klaten, Central Java
11	Industrial Waste	Rungkut, Surabaya, East Java
12	Typic Rhodudalf	Pathuk, Gunung Kidul, Central Java
13	Typic Rhodudult	Jasinga, Bogor, West Java
14	Agricultural Waste	Fakultas Peternakan, UGM, Yogyakarta
15	Typic Udipsamment	Balecatur, Sleman, Central Java
16	Lithic Udorthent	Gunung Cekel, Kulon Progo, Central Java
17	Entic Chromudert	Sedayu, Kulon Progo, Central Java
18	Lithic Udorthent	Sedayu, Kulon Progo, Central Java
19	Entic Pelludert	Sedayu, Kulon Progo, Central Java
20	Waste mushroom factory	Jerami Padi, Kulon Progo, Central Java
21	Compost	Mushroom factory, Dieng, Central Java

Table 2b. **Some chemica; properties of the material used**

nr.	Moisture Content (% w/w)	$pH(H_2O)$	pH(KCl)	R exch. Ca + K + Na (meq/100 g dry)
1	7.17	6.7	5.5	8.17
2	7.53	4.3	3.4	1.29
3	10.01	6.9	5.8	26.16
4	1.83	6.1	4.9	3.97
5	68.52	3.1	2.0	3.68
6	257.14	5.4	4.6	25.21
7	6.95	5.7	4.8	3.36
8	5.04	7.6	6.9	15.67
9	10.01	5.5	4.7	1.19
10	10.38	6.0	5.9	7.69
11	4.17	6.2	6.1	9.06
12	4.38	5.3	4.4	4.12
13	10.25	4.3	3.3	0.21
14	8.58	7.1	6.8	15.13
15	2.15	6.1	4.9	4.42
16	3.09	6.4	3.7	10.45
17	7.30	6.8	5.4	16.05
18	6.61	7.6	6.9	20.81
19	11.73	7.5	6.3	23.17
20	8.70	8.7	8.0	49.18
21	9.89	8.7	7.8	43.98

Table 3. **Settings of the programme used for the titration of dichromate with ferrous ions (end point titration with Titrator Radiometer TTT85)**

Parameter	Value
1 st end point	700 mV
dynamic range	1000 mV
2 nd end point	---
delay	5 s
pre dose	0.00 ml
sample volume	1.00 ml
titrant concentration	1.000
unit	M
blank volume	0.00 ml
maximum volume	20.00 ml

Table 4. **Carbon determinations (C_t) for compost (10 replicates)**

Titration With Diphenylamine	Automatic Redox Titration
21.12	20.35
23.60	20.98
21.48	20.96
21.48	20.91
21.43	19.48
21.07	20.45
23.15	20.47
21.43	20.68
21.12	21.03
23.15	20.99
(21.90 = 0.98)	(20.63 = 0.48)

Table 5. **Organic matter determinations with the two different procedures**

nr.	Titrimetric				Potentiometric			
	% O.M.			(Mean ± s)	% O.M.			(Mean ± s)
1	4.06	4.06	4.14	4.09 ± 0.05	3.54	3.49	3.58	3.54 ± 0.05
2	5.09	4.93	5.09	5.04 ± 0.09	4.67	4.76	4.96	4.80 ± 0.15
3	3.42	3.34	3.34	3.37 ± 0.05	2.85	3.07	3.08	3.00 ± 0.13
4	1.99	1.99	1.92	1.97 ± 0.04	1.43	1.50	1.43	1.45 ± 0.04
5	125.14	129.22	127.86	127.41 ± 2.08	116.08	120.02	116.96	117.69 ± 2.07
6	99.58	96.56	99.58	98.57 ± 1.74	81.26	83.82	80.32	81.80 ± 1.81
7	2.83	2.83	2.83	2.83 ± 0.00	1.84	2.15	2.14	2.04 ± 0.18
8	2.66	2.66	2.83	2.72 ± 0.10	2.20	2.20	2.13	2.18 ± 0.04
9	22.84	22.84	22.54	22.74 ± 0.17	18.22	17.78	18.54	18.18 ± 0.38
10	105.46	106.36	106.36	106.06 ± 0.52	92.44	97.18	94.76	94.79 ± 2.05
11	25.55	25.96	26.37	25.96 ± 0.41	23.77	25.94	24.95	24.89 ± 1.09
12	3.18	3.09	3.26	3.18 ± 0.09	2.25	2.21	2.52	2.33 ± 0.17
13	3.32	3.23	3.41	3.32 ± 0.09	2.57	2.53	2.68	2.59 ± 0.08
14	66.76	65.02	67.64	66.47 ± 1.33	73.52	69.42	71.24	71.39 ± 2.05
15	2.99	2.99	2.99	2.99 ± 0.00	1.63	1.67	1.58	1.63 ± 0.05
16	1.68	1.68	1.51	1.62 ± 0.10	1.06	0.86	0.99	0.97 ± 0.10
17	3.66	3.66	3.75	3.69 ± 0.05	3.16	3.15	3.13	3.15 ± 0.02
18	4.57	4.66	4.48	4.57 ± 0.09	4.64	4.45	4.25	4.45 ± 0.20
19	2.29	2.29	2.11	2.23 ± 0.10	2.63	2.63	2.70	2.65 ± 0.04
20	56.60	57.48	59.26	57.78 ± 1.36	56.88	54.78	54.86	55.51 ± 1.19
21	42.14	42.86	42.86	42.62 ± 0.25	40.89	40.93	41.35	41.06 ± 0.42

Table 6. **Conversion factors for organic material**

nr.	Ash Content (% w/w)	% O.M. (1)	% C_t (2)	C_t/O.M.
5	0.11	99.89	58.85	0.59
6	9.89	90.11	40.90	0.45
10	24.56	75.44	47.40	0.63
14	43.00	57.00	35.70	0.63
20	47.09	52.91	27.76	0.52
21	54.34	45.66	20.53	0.45

(1) % O.M. = (100 — ash content) %

(2) % C_t = (0.5 × O.M. [*table 5, potentiometric, mean*]) %.

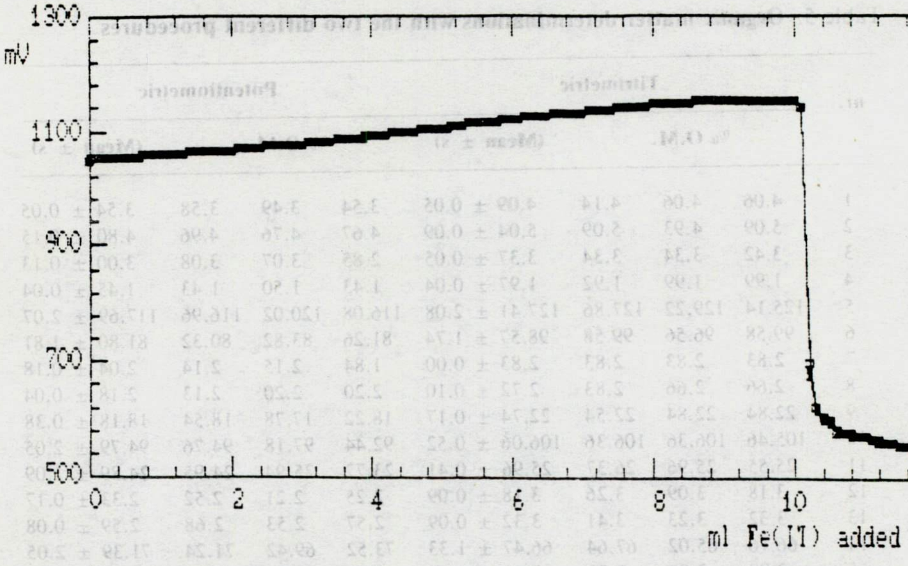

Figure 1. **Change in potential during the potetiometric titration of the excess of dichromate with ferrous ions**

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