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Liming material — Determination of neutralizing value — Titrimetric methods

Amendements minéraux basiques — Détermination de la valeur neutralisante — Méthodes par titrimétrie

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Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This method has been developed to assess the ability of a product to deliver potential neutralization capacity, i.e. to neutralize protons or acidic cations in soils and consequently maintain or increase its pH. It relies on the measurement of hydrochloric acid consumption when a liming material is mixed in solution with hydrochloric acid in excess.

Two different procedures are described (method A and method B) because the titration to pH 7,0 is not applicable to silicate liming materials due to the precipitation of compounds at this pH value.

In method B, the turning point at pH 4,8 on the titration curve is taken as the end-point of the titration. For carbonaceous liming materials the difference in the consumption of sodium hydroxide solution for back titration between the titration end-points of pH 4,8 and pH 7,0 is negligible.

This document derives from the European standard EN 12945:2014+A1. However, its principle is the same as in AOAC 955.01 and BNQ 0419-070: 2011.

The following changes have been made to the EN 12945:2014+A1 edition:

- expression of results is allowed as $CaCO_3$ equivalent, not only as CaO or HO^- equivalents;
- Annex B has been completed accordingly to present all the necessary conversion tables;
- a new ISO international ring test was performed in 2017 to determine precision data (see Clause 10)
- Annex A was revised accordingly.

Liming material — Determination of neutralizing value — Titrimetric methods

1 Scope

This document specifies two methods for the determination of the neutralizing value (NV) of liming materials.

Method A is applicable to all liming materials except silicate liming materials.

NOTE 1 Examples of hard liming materials are limestone and dolomite. Examples of soft liming materials are chalk, marl and burnt lime.

Method B is applicable to all liming materials.

Neither method correctly takes into account the potential neutralizing value of material containing more than 3 % P_2O_5. For a more accurate agronomic assessment of products containing more than 3 % P_2O_5, EN 14984[8] is used to determine the liming efficiency.

NOTE 2 The methods described in ISO 6598 and ISO 7497 can be used for the determination of P_2O_5 content. Further information on P analyses is given in References [5] and [6].

NOTE 3 Carbonate consumes H^+ and removes acidity in solution with subsequent dissociation to H_2O and CO_2. Forms of orthophosphate can consume H^+ but are not dissociated to molecular forms that remove acidity. The acidity is back titrated with alkali causing an underestimation of NV.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 8157, *Fertilizers and soil conditioners — Vocabulary*

ISO 14820-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8157 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Dissolution of the sample in a specified quantity of hydrochloric acid standard solution. Determination of the excess acid by back titration with a sodium hydroxide standard solution.

For products containing iron, a preliminary oxidization is necessary in method B.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

NOTE Commercially available solutions can be used.

5.1 **Water**, according to ISO 3696, grade 3.

5.2 **Hydrochloric acid standard solution**, *c*(HCl) = 0,5 mol/l.

This solution can be purchased from a chemical supply company certified to have a concentration within a 0,4 % variance (0,498 M to 0,502 M).

If preparing from concentrated HCl, determine the exact concentration of the solution by titration with sodium hydroxide standard solution (5.3) using phenolphthalein solution (5.4) as indicator.

Apply the appropriate correction factor in the calculation of the results (see Clause 9).

In case of any doubt about the concentration of the HCl solution, measuring the neutralizing value of a precipitated calcium carbonate (PCC, 5.6) is recommended.

5.3 **Sodium hydroxide standard solution**, *c*(NaOH) = 0,25 mol/l.

This solution can be purchased from a chemical supply company certified to have a concentration within a 0,2 % variance (0,249 5 M to 0,250 5 M).

If preparing from NaOH pellets, determine the exact concentration of the standard solution by titration against approximately 2 g of dried potassium hydrogen phthalate ($KHC_8H_4O_4$), weighed to the nearest 0,001 g.

The solution shall be stored in a polyethylene bottle and absorption of carbon dioxide during storage should be avoided.

NOTE 1 ml of 0,25 mol/l sodium hydroxide solution is equivalent to 51,055 mg of potassium hydrogen phthalate.

Apply the appropriate correction factor in the calculation of the results (see Clause 9).

In case of any doubt about the concentration of the NaOH solution, measuring the neutralizing value of a precipitated calcium carbonate (PCC, 5.6) is recommended.

5.4 **Phenolphthalein indicator solution**.

Dissolve 0,25 g of phenolphthalein in 150 ml of ethanol with a mass fraction of 93 % and dilute with water to 250 ml.

The phenolphthalein solution (5.4) is a colour indicator to determine when the end point pH is reached and is only suitable in Method A with an end point pH of 7. The indicator is not required if a pH electrode is used to monitor end point pH.

NOTE If there is a buffering capacity in the sample, a deviation can occur between phenolphthalein indicator solution (changes at pH 8,3) and pH end point with pH meter (7,0).

5.5 **Hydrogen peroxide solution**.

Dilute one volume of hydrogen peroxide [ρ (H_2O_2) = 30 g/100 ml] with four volumes of water.

Hydrogen peroxide is used in Method B to oxidize any reduced iron in slag liming materials.

5.6 Precipitated calcium carbonate.

Precipitated calcium carbonate of recognized analytical grade, minimum 99 % $CaCO_3$.

Quality control check by using precipitated calcium carbonate and blank solution should be used in each series of measurements.

6 Apparatus

Usual laboratory apparatus and, in particular, the following.

6.1 Test sieve, conforming to the requirements of ISO 3310-1, of maximum aperture size 250 µm.

6.2 pH meter, minimum sensitivity 0,05 pH units, with a suitable glass electrode and a calomel or other reference electrode or a combined electrode, calibrated using two buffer solutions whose pH values cover the range pH 4 to pH 7.

A pH meter is not required if using phenolphthalein to determine end point pH of 7 in Method A.

6.3 Mechanical stirrer, e.g. magnetic stirrer.

6.4 Desiccator.

7 Sampling

Sampling is not part of the method specified in this document. Recommended sampling methods are described in ISO 14820-1 and ISO 14820-3 .

Prepare the sample of the liming materials in accordance with ISO 14820-2.

8 Procedure

8.1 Preparation of the test sample

Dry the test sample at (105 ± 2) °C to constant mass. Record the as-received (m_w) and dry (m_d) masses. Grind the sample so that it passes the 250 µm test sieve (6.1).

NOTE A smaller sieve size depending on material type can be used such as 150 µm/Mesh 100 for slags.

Mix thoroughly.

Perform the following when titration is not processed immediately.

- In case of burnt lime, store the prepared test sample in a desiccator (6.4) until the effective measurement.
- Otherwise, store the prepared test sample in a waterproof plastic bag.

8.2 Determination

8.2.1 Method A

8.2.1.1 Test portion

Weigh about 0,5 g, to the nearest 0,001 g, of burnt or hydrated lime or 1 g of ground limestone or ground marl (prepared according to 8.1) into a 250 ml suitable flask.

8.2.1.2 Titration

Add 50 ml of the hydrochloric acid standard solution (5.2) with continuous shaking and boil gently for 5 min (10 min for hard materials) using boiling granules.

Cool down to 20 °C to 25 °C. Add a few drops of phenolphthalein solution or insert pH and reference electrodes (6.2) into the solution. Stir (6.3) the solution.

Titrate with the sodium hydroxide standard solution (5.3) with moderate stirring (avoid splashing) until a pH of 7,0 or pink colour of phenolphthalein are stable for 1 min while stirring is maintained.

8.2.2 Method B

8.2.2.1 Test portion

Weigh about 0,5 g, to the nearest 0,001 g, of the prepared test sample (8.1) into a 250 ml suitable flask.

8.2.2.2 Titration

Rinse the inside walls of the flask with 10 ml of water.

Add 35 ml of the hydrochloric acid standard solution (5.2) with continuous shaking.

Heat and boil gently for 10 min to dissolve the sample using boiling granules. Stir continuously. Cool down to between 20 °C to 25 °C, then dilute with water to about 100 ml.

Add 5 ml of hydrogen peroxide solution (5.5).

NOTE Ferrous ions from silicate liming materials can oxidize and consume OH^- during titration. To avoid OH^- consumption by ferrous ions, hydrogen peroxide is added which forms ferric and ferrous ions in a neutral reaction.

Transfer quantitatively into a 200 ml graduated flask; make up the volume with water and mix. Pass through a dry filter into a dry container, discarding the initial portion. Pipette an aliquot portion of 100 ml of the solution into a 250 ml beaker.

Insert the electrodes of the pH meter (6.2) and a stirrer (6.3).

Titrate with the sodium hydroxide standard solution (5.3) with moderate stirring (avoid splashing) until a pH of 4,8 is stable for 1 min (while stirring is maintained).

9 Calculation and expression of results for method A and method B

9.1 Calculate the neutralizing value of the dried product, N_d, according to Formula (1):

$$N_d = \frac{c \times (M_1 \times V_1 \times f_1 \times A - M_2 \times V_2 \times f_2) \times 100}{m_t \times A} \qquad (1)$$

where

c is the factor to convert hydrochloric acid standard solution into CaO or $CaCO_3$ or HO^- equivalent;

$c = 0{,}028$ when neutralizing value should be expressed as CaO

$c = 0{,}050$ when neutralizing value should be expressed as $CaCO_3$

$c = 0{,}017$ when neutralizing value should be expressed as HO^-

M_1 is the molarity of hydrochloric acid standard solution (5.2), in mol/l;

V_1 is the total volume of hydrochloric acid standard solution (5.2), in millilitres;

f_1 is the factor of hydrochloric acid standard solution (5.2);

A is equal to 1 for method A, and the factor of the taken aliquot is 0,5 for method B;

M_2 is the molarity of sodium hydroxide standard solution (5.3), in mol/l;

V_2 is the volume of sodium hydroxide standard solution (5.3), in millilitres;

f_2 is the factor of sodium hydroxide standard solution (5.3);

m_t is the mass of the test portion in the aliquot portion taken, in grams.

9.2 Calculate the neutralizing value of the “as-received” product, N_{ar}, according to Formula (2):

$$N_{ar} = \frac{N_d\, m_d}{m_w} \tag{2}$$

where

N_d is the neutralizing value of the dried sample;

m_d is the mass of the sample after drying, in grams;

m_w is the mass of the sample before drying, in grams.

The result shall be taken as the arithmetic mean of at least two determinations.

If the difference between the two results seems higher than expected, check good manufacturing laboratory practice.

Expressions of results do not contain any correction factor to take into account material with a content of P_2O_5 higher than 3 %.

According to the required unit of expression, and as specified under d) in Clause 11, the result of neutralizing value measurement shall be expressed as follows:

xx (eq CaO) and/or yy (eq $CaCO_3$) and/or zz (eq HO^-).

10 Precision

10.1 General

The precision of the method was established by an inter-laboratory trial carried out in 2017 in accordance with ISO 5725:1994 with 8 laboratories worldwide.

The values obtained for repeatability limit and reproducibility limit are expressed for the 95 % probability level are not applicable to concentration ranges and matrices other than those given.

According to the method, each elementary result is the mean of 2 measurements.

According to the ISO procedure to calculate r and R values, 4 repetitions were made.

Suspect values, obviously out of range, due to method errors, bad reporting or bad final calculation have been considered as outliers and consequently removed before r and R calculation.

Gypsum is not a liming material. It has a calcium content, but it has no neutralizing value. This product was however included in the interlaboratory trial to show that the method, though rather unprecise for this material with values nearby zero, is anyway able to detect an absence of neutralizing value.

NOTE The repeatability limits and reproducibility limits obtained from the inter-laboratory trial for each product being tested are given in Annex A.

10.2 Repeatability

The absolute difference between two independent single test results, obtained using the same method, on identical test material, in the same laboratory, by the same operator, using the same equipment, within the shortest feasible time interval, exceeds the repeatability limit (*r*) on average not more than once in 20 cases in the normal and correct operation of the method.

The repeatability value r is depending on the tested material and is given in Table 1 below.

Table 1 — Repeatability limits (*r*) for neutralizing value measurement

Level (Material)	CaO (%)	MgO (%)	Number of laboratories	Mean NV (CaO eq.)	Std. Dev. (%)	r (abs.)	r (rel.) (%)
A PCC CaCO3 Control	55,60	0,01	8	55,9	0,445	0,799	1,430
B MgO Control	0,22	99,86	8	132,9	0,215	0,919	0,692
C Limestone	54,10	0,49	7	55,0	0,404	0,714	1,298
D Dolomite	31,25	20,41	8	58,8	0,553	1,046	1,778
E Burnt lime	91,84	0,52	8	88,7	1,860	5,304	5,980
F Chalk	48,79	0,35	8	51,9	0,366	0,610	1,176
G Wood ashes	42,42	3,69	8	48,1	0,984	1,530	3,181
H Sugar factory lime	46,43	2,32	8	47,1	0,609	0,922	1,959
I CaCO3 from paper industry	41,56	1,78	8	50,5	0,689	1,119	2,214
J BOF Slags	47,88	4,82	7	55,7	0,954	1,707	3,064
K Gypsum	31,98	0,04	8	1,0	13,194	0,413	42,414
L Mixed product	35,14	4,04	7	44,1	0,738	1,045	2,369

10.3 Reproducibility

The absolute difference between two independent single test results, obtained using the same method, on identical test material, in different laboratories, with different operators using different equipment, will exceed the reproducibility limit (*R*) on average not more than once in 20 cases in the normal and correct operation of the method.

The reproducibility value R is depending on the tested material and is given in Table 2 below.

Table 2 — Reproducibility limits (*R*) for neutralizing value measurement

Level (Material)	CaO (%)	MgO (%)	Number of laboratories	Mean NV (CaO eq.)	Std. Dev. (%)	R (abs.)	R (rel.) (%)
A PCC CaCO3 Control	55,60	0,01	8	55,9	0,445	1,768	3,165
B MgO Control	0,22	99,86	8	132,9	0,215	2,677	2,014
C Limestone	54,10	0,49	7	55,0	0,404	1,522	2,765
D Dolomite	31,25	20,41	8	58,8	0,553	1,654	2,811
E Burnt lime	91,84	0,52	8	88,7	1,860	16,431	18,526
F Chalk	48,79	0,35	8	51,9	0,366	4,810	9,269
G Wood ashes	42,42	3,69	8	48,1	0,984	6,766	14,069
H Sugar factory lime	46,43	2,32	8	47,1	0,609	2,248	4,778
I CaCO3 from paper industry	41,56	1,78	8	50,5	0,689	12,156	24,050
J BOF Slags	47,88	4,82	7	55,7	0,954	8,146	14,618
K Gypsum	31,98	0,04	8	1,0	13,194	2,098	215,486
L Mixed product	35,14	4,04	7	44,1	0,738	5,140	11,657

11 Test report

The test report shall contain at least the following information:

a) all data necessary for the identification of the sample;

b) a reference to this document, i.e. ISO 20978:2020;

c) the method used (method A or method B);

d) the results and the units in which the results have been expressed;

e) any particular points observed in the course of the test;

f) optionally a statement that correction factors for materials containing more than 3 % P_2O_5 are not included;

g) any operations not specified in the method or regarded as optional which might have affected the results.

Annex A
(informative)

Results of an interlaboratory trial to determine the neutralizing value

An interlaboratory trial was organized in 2017 by ISO/TC 134/WG 4 to obtain precision data for the method specified in this document.

In this trial, 8 laboratories from 5 participating countries determined the neutralizing value of 12 types of product. The values derived from this interlaboratory trial for the repeatability limit and reproducibility limit of each product being tested are given in Table A.1.

Table A.1 — Repeatability limits and reproducibility limits derived from interlaboratory trial

Neutralizing Value Level (Material)	CaO (%)	MgO (%)	Nb. of laboratories	Mean (CaO eq.)	Std. Dev. (%)	r (abs.)	R (abs.)	r (%)	R (%)
A PCC CaCO3 Control	55,60	0,01	8	55,9	0,445	0,799	1,768	1,430	3,165
B MgO Control	0,22	99,86	8	132,9	0,215	0,919	2,677	0,692	2,014
C Limestone	54,10	0,49	7	55,0	0,404	0,714	1,522	1,298	2,765
D Dolomite	31,25	20,41	8	58,8	0,553	1,046	1,654	1,778	2,811
E Burnt lime	91,84	0,52	8	88,7	1,860	5,304	16,431	5,980	18,526
F Chalk	48,79	0,35	8	51,9	0,366	0,610	4,810	1,176	9,269
G Wood ashes	42,42	3,69	8	48,1	0,984	1,530	6,766	3,181	14,069
H Sugar factory lime	46,43	2,32	8	47,1	0,609	0,922	2,248	1,959	4,778
I CaCO3 from paper industry	41,56	1,78	8	50,5	0,689	1,119	12,156	2,214	24,050
J BOF Slags	47,88	4,82	7	55,7	0,954	1,707	8,146	3,064	14,618
K Gypsum	31,98	0,04	8	1,0	13,194	0,413	2,098	42,414	215,486
L Mixed product	35,14	4,04	7	44,1	0,738	1,045	5,140	2,369	11,657

Annex B
(informative)

Conversion tables

Tables B.1 to B.6 give the conversion factors between CaO, $CaCO_3$ and HO^-.

— Table B.1: CaO to HO^- $HO^- = CaO \times 0{,}606\ 56$

— Table B.2: HO^- to CaO $CaO = HO^-/0{,}606\ 56$

— Table B.3: $CaCO_3$ to CaO $CaO = CaCO_3 \times 0{,}560\ 29$

— Table B.4: CaO to $CaCO_3$ $CaCO_3 = CaO/0{,}560\ 29$

— Table B.5: $CaCO_3$ to HO^- $HO^- = CaCO_3 \times 0{,}339\ 85$

— Table B.6: HO^- to $CaCO_3$ $CaCO_3 = HO^-/0{,}339\ 85$

The converting factors are only depending on charge and mass of elements, considered with five significant digits.

In Tables B.1 to B.6, the values are calculated with five digits after the decimal place and then rounded to two digits after the decimal place.

Table B.1 — CaO → HO^-

CaO	HO^-	CaO	HO^-	CaO	HO^-
15	9,10	50	30,33	85	51,56
16	9,70	51	30,93	86	52,16
17	10,31	52	31,54	87	52,77
18	10,92	53	32,15	88	53,38
19	11,52	54	32,75	89	53,98
20	12,13	55	33,36	90	54,59
21	12,74	56	33,97	91	55,20
22	13,34	57	34,57	92	55,80
23	13,95	58	35,18	93	56,41
24	14,56	59	35,79	94	57,02
25	15,16	60	36,39	95	57,62
26	15,77	61	37,00	96	58,23
27	16,38	62	37,61	97	58,84
28	16,98	63	38,21	98	59,44
29	17,59	64	38,82	99	60,05
30	18,20	65	39,43	100	60,66
31	18,80	66	40,03	101	61,26
32	19,41	67	40,64	102	61,87
33	20,02	68	41,25	103	62,48
34	20,62	69	41,85	104	63,08
35	21,23	70	42,46	105	63,69

Table B.1 *(continued)*

CaO	HO^-	CaO	HO^-	CaO	HO^-
36	21,84	71	43,07	106	64,30
37	22,44	72	43,67	107	64,90
38	23,05	73	44,28	108	65,51
39	23,66	74	44,89	109	66,12
40	24,26	75	45,49	110	66,72
41	24,87	76	46,10	111	67,33
42	25,48	77	46,71	112	67,93
43	26,08	78	47,31	113	68,54
44	26,69	79	47,92	114	69,15
45	27,30	80	48,52	115	69,75
46	27,90	81	49,13	116	70,36
47	28,51	82	49,74	117	70,97
48	29,11	83	50,34	118	71,57
49	29,72	84	50,95	119	72,18
50	30,33	85	51,56	120	72,79

$HO^- = CaO \times 0{,}606\,56$

Table B.2 — $HO^- \rightarrow CaO$

HO^-	CaO	HO^-	CaO
10	16,49	45	74,19
11	18,14	46	75,84
12	19,78	47	77,49
13	21,43	48	79,13
14	23,08	49	80,78
15	24,73	50	82,43
16	26,38	51	84,08
17	28,03	52	85,73
18	29,68	53	87,38
19	31,32	54	89,03
20	32,97	55	90,68
21	34,62	56	92,32
22	36,27	57	93,97
23	37,92	58	95,62
24	39,57	59	97,27
25	41,22	60	98,92
26	42,86	61	100,57
27	44,51	62	102,22
28	46,16	63	103,86
29	47,81	64	105,51
30	49,46	65	107,16
31	51,11	66	108,81
32	52,76	67	110,46
33	54,41	68	112,11
34	56,05	69	113,76

Table B.2 *(continued)*

HO^-	CaO	HO^-	CaO
35	57,70	70	115,40
36	59,35	71	117,05
37	61,00	72	118,70
38	62,65	73	120,35
39	64,30	74	122,00
40	65,95	75	123,65
41	67,59	76	125,30
42	69,24	77	126,95
43	70,89	78	128,59
44	72,54	79	130,24
45	74,19	80	131,89

$CaO = HO^- / 0{,}606\,56$

Table B.3 — $CaCO_3$ → CaO

$CaCO_3$	CaO	$CaCO_3$	CaO	$CaCO_3$	CaO	$CaCO_3$	CaO	$CaCO_3$	CaO
25	14,01	60	33,62	95	53,23	130	72,84	165	92,45
26	14,57	61	34,18	96	53,79	131	73,40	166	93,01
27	15,13	62	34,74	97	54,35	132	73,96	167	93,57
28	15,69	63	35,30	98	54,91	133	74,52	168	94,13
29	16,25	64	35,86	99	55,47	134	75,08	169	94,69
30	16,81	65	36,42	100	56,03	135	75,64	170	95,25
31	17,37	66	36,98	101	56,59	136	76,20	171	95,81
32	17,93	67	37,54	102	57,15	137	76,76	172	96,37
33	18,49	68	38,10	103	57,71	138	77,32	173	96,93
34	19,05	69	38,66	104	58,27	139	77,88	174	97,49
35	19,61	70	39,22	105	58,83	140	78,44	175	98,05
36	20,17	71	39,78	106	59,39	141	79,00	176	98,61
37	20,73	72	40,34	107	59,95	142	79,56	177	99,17
38	21,29	73	40,90	108	60,51	143	80,12	178	99,73
39	21,85	74	41,46	109	61,07	144	80,68	179	100,29
40	22,41	75	42,02	110	61,63	145	81,24	180	100,85
41	22,97	76	42,58	111	62,19	146	81,80	181	101,41
42	23,53	77	43,14	112	62,75	147	82,36	182	101,97
43	24,09	78	43,70	113	63,31	148	82,92	183	102,53
44	24,65	79	44,26	114	63,87	149	83,48	184	103,09
45	25,21	80	44,82	115	64,43	150	84,04	185	103,65
46	25,77	81	45,38	116	64,99	151	84,60	186	104,21
47	26,33	82	45,94	117	65,55	152	85,16	187	104,77
48	26,89	83	46,50	118	66,11	153	85,72	188	105,33
49	27,45	84	47,06	119	66,67	154	86,28	189	105,89
50	28,01	85	47,62	120	67,23	155	86,84	190	106,46
51	28,57	86	48,18	121	67,80	156	87,41	191	107,02
52	29,14	87	48,75	122	68,36	157	87,97	192	107,58
53	29,70	88	49,31	123	68,92	158	88,53	193	108,14