2013-38

(2013\5\5)

(1)

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(2)

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.   :   1-2

.   :   2-2

.   :   3-2

:   4-2

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:   5-2

.   /

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:   6-2

.(1)   (1-3-)

: 25-2

(23) .

(3)

(1)

. " " .

(4)

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(5)

(15)

.

(6)

(9)   1-6

:

:   (N)   ( )

. (P, K)   (   )

. (P_2O_5, K_2O) (   )

.   (   )

(172)   (3)

:

$$0.436 \times (P_2O_5) \qquad = (P) \qquad\qquad ()$$

$$0.830 \times (K_2O) \qquad = (K) \qquad\qquad ( )$$

2-6

)

: $\qquad\qquad ((17$

… (CaO, MgO, Na_2O, SO_3) $\qquad\qquad$ ()

… (Ca, Mg, Na, S) $\qquad\qquad$ ( )

.$\qquad\qquad$ ( )

:

$$0.715 \times (CaO) \qquad = (Ca) \qquad\qquad ()$$

$$0.603 \times (MgO) \qquad = (Mg) \qquad\qquad ( )$$

$$0.742 \times (Na_2O) \qquad = (Na) \qquad\qquad ( )$$

$$0.400 \times (SO_3) \qquad = (S) \qquad\qquad ( )$$

.

) $\qquad\qquad\qquad\qquad$ 3-6

(

(1) ( ) ( ) ( ) ()

:

-) (2-2-) $\qquad\qquad\qquad\qquad$ ()

.(1) $\qquad$ (3-2

( ) ( ) ( ) () $\qquad\qquad\qquad$ ( )

.(1)

4-6

(Ca, Mg, Na, S) $\qquad$ (N, P, K)

.(1) $\qquad$ (3-2-) (2-2-)

: $\qquad\qquad\qquad\qquad$ 5-6

(1)   (1-)   ()

                                    .   (6)

                                                                                    ( )

    (1)   (1-2-)

( )   ( )   ()

                                                    :   (1)   ( )

              .   (1)

                                                                         (2)

                      .

                            "   " "   "

                              (1)   (3-)

                                    .

(7)

        .(9)   1-7

                                                                          2-7

          .   .

(8)

                                                (3-26)

                            .

(9)

: ((7))

.

" " -

.(1) -

" " -

.(23) (21) (19) -

-

(K) (P₂O₅) (P) (N)

(Mg) (CaO) (Ca) (K₂O)

(Na₂O) (Na) (MgO)

(Co) (Cu) (B) (SO₃) (S)

.(Zn) (Mo) (Mn) (Fe)

-

:

".…. " (1)

.(1) (1-3-)

".…. " (2)

.(1) (2-3-)

.B, Co, Cu, Fe, Mn, Mo, Zn -

(2-) (1-) -

.(1)

-

.

/)

. (/

( ) -

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.(1)   -

                                                                                                      -

.(1)   (2-)   (1-)

                                                                                                      -

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.   -

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(1-9)   2-9

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                                                                                                     3-9

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(10)

                                                                                                    1-10

(9)   .

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(1-10)   2-10

.

(2-7)   3-10

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(11)

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(12)

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(13)

1-13   (2)

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2-13   (2)

.

3-13   .(1)

(14)

(1)   :

( )

( )   .(   )

( )

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(15)

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(16)

)

(/)

.(1) (3-2-) (2-2-) ( ) ( ) ()

(17)

(1) ( ) ( ) ()

:

. %1.4 (CaO) %2 ()

. %1.2 (MgO) %2 ( )

. %2.2 (Na$_2$O) %3 ( )

. %2 (SO$_3$) %5 ( )

(2-19) (2)

.

(18)

1-18

: (1) ( ) ( ) ()

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( )

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( )

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(1)   ( )

.

(19)

1-19   ( )   (1-9)

.(6-19)   (5-19)   (4-19)   (3-19)   (2-19)

2-19   :

(1)

.

(2)

.

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3-19

4-19   "   "   " "

/   .

5-19

.

:   (N)   / (P₂O₅)

(P)   / (K₂O)   (K).   :

/ (CaO)   (Ca)   / (MgO)   (Mg)

/ (Na₂O)   (Na)   / (SO₃)   (S).

(2-2-)   (3-2-)

(1)   .

(172)   (10)

(1)

.

(2-2-)   (3-2-)   (1).

(20)

)

(3-2   (1).   (( )   (2-2-)   (-

(21)

( )   (1-9)

(2-21)   (3-21)   (4-21)   (5-21).

"   "   " "

/

(2-2-)   (3-2-)   (1) .

.

:

(CaO) /   (Ca)   (MgO) /   (Mg)

(Na₂O) /   (Na)   (SO₃) /   (S).

(1)

.

(2-2-)   (3-2-)   (1).

(1) .

(22)

(   )

(1-) (1-2-)   (1) .

(23)

1-23   ()   (1-9)

(2-23)   (3-23)   (4-23)   (5-23) .

2-23

"   "

.

3-23   (1-)

(1)

.

4-23

(1)

.

(1-2-)

(1) .

5-23

(1-) (1-2-)   (1) : "

.   . "

(24)

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(25)

(   )

28%

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(26)

26-1

(3).

26-2

(3).

26-3

.

(27)

(26)

(2)

(3)   (1)   (3)   (3).

(1-30)   (1-33)

5   5   )

.(

.

(28)

.

(29)

1-29

.

2-29

(1)

(3)   (4).

3-29

/

(3)   (4)

(2).

(30)

.

(31)

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(32)

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(1)

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1 –

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(1)
(2)
(3)
(4)
(5)
(6)

- ( )

- -

6	5	4	3	2	1
:		%15		( )	( )1
			)		
			(		
		%1.5 :			

(172)   (16)

6	5	4	3	2	1
		%13 : %5		( )	( )1
	" "	%10 %14			( )1
		%15		) (	( )2
		%15	Caliche		( )2

6	5	4	3	2	1
		%18 %75	) (		3( )
	"	%18 %75 : %1 : - %3 : -	) (+		3( )
( )	( ) ") %15 ("	%19.7 %2.2 ( )	) %15 ( )		4

6	5	4	3	2	1
	" ") (/ ( ) . %20 %90	%2 (1-3) (2-3)			5
		%25 . %5			6
		%19 . . %6			7

6	5	4	3	2	1
		%5			
		%19 . . %6	) /		8
		%5			
		%44) .(%1.2	( )		9
%1) (Crotonylidene diurea		%28 %25 Crotonylidene diurea %3	crotonaldehyde .Monomeric compound		10

6	5	4	3	2	1
%1) (Isobutylidene diurea		%28 %25 Isobutylidene diurea %3	-2		11
%1) (		%36 3/5 %31 %5			12

6	5	4	3	2	1
		%18	Crotonylidene diurea	Crotonylidene diurea	13
: %1		%3	( )3 1-)		
-		/ /	(5 ( )3		
-		1/3			
-					
Crotonylidene diurea		Crotonylidene diurea			
		:			
		+)			
		× (Crotonylidene diurea 0.026			

6	5	4	3	2	1
		%18	Isobutylidene diurea	Isobutylidene diurea	14
: %1		%3	1-)		
-		/ /	(5 ( )3 ( )3		
-		1/3			
-					
Isobutylidene		Isobutylidene diurea			
Diurea					
		:			
		+)			
		× (Isobutylidene diurea 0.026			

6	5	4	3	2	1
		%18			15
: %1		%3	1-)		
-		/ /	(5 ( )3 ( )3		
-		1/3			
-					
		3/5			
		:			
		+)			
		$0.026 \times ($			

6	5	4	3	2	1
		%30			16
		%4			
		%12			
		%0.9			

.   (7 6 5 4 3 1   )

:

(1)

(2)

(3)

-                              - (   )   (4)

(5)

-                    -   (6)

6	5	4	3	2	1
) (%2 %75		%12 %75 %2 %2 : %75 - 0.16 %96 - 0.63		: - -	1
		%16 %93 1 :			()2

6	5	4	3	2	1
		%25 %93 1 :			( )2
		%38 %85 3 :			( )2

6	5	4	3	2	1
) (		%20 %40 : - 90% 0.16 - 98% 0.63			3
) (		%16 %6 %40 : - 90% 0.16 - 98% 0.63			3( )

6	5	4	3	2	1
		%38			4
		:			
		%90 -			
		0.16			
		%98 -			
		0.63			
		%25			5
		:			
		%75 -			
		0.16			
		%96 -			
		0.63			

6	5	4	3	2	1
) (		%30 %75 : %90 - 0.16 %98 - 0.63			6
) (%2 0.063		%25 %55 : %90 - 0.063 %99 - 0.125			7

:

(1)
(2)
(3)
(4)   - (   )   -
(5)
(6)   -   -

6	5	4	3	2	1
		%10			1
		%5			
		%18			2
%5					

(172)   (32)

6	5	4	3	2	1
		%37			3
		%37 %5			4
		%47 %3			5

6	5	4	3	2	1
		%22 %8 %3			6
		%8 %6 + %20 : %3			7

	:	1-1-
(+ +) %20 : -	:( )	
%5 %5 %3 : -		

	6 5 4				
K₂O	P₂O₅	N	K₂O	P₂O₅	N
6	5	4	3	2	1

K₂O / 6	P₂O₅ / 5	N / 4	3	P₂O₅ / 2	N / 1
(1)	(1)	(1)		(1)	(1)
		(2)			(2)
" " (2)		(2)		(2)	(3)
%2		%1 (5)			
		( )			(4)
(3)				(3)	(5)
		(3)			
:(3) (2) (1)					
-		%28		(4)	

	%2	(2-3)			
	(2)			(5)	
	-				
	%2			(-6)	
	(3)				
				%75	
	((1))				
				%2	
	%2				
	1			(-6)	
(3) (2)				%2	
	1				
	(-2)			(7)	
				%75	
	.				
	(1)			(8)	
	(4) (3)				
				%55	

(172)   (36)

	:				
	%2 -			%2	
	((4))				
	%5 -				
	)				
	((3)				
	%2.5 -				
	((1))				
	"				
"					
	"				
."					
	(-2)				
(3)					
	3				
	(-2)				

	.				
	(7) (1)				
	.				
	:				
	%2 –				
	((1))				
	%5 –				
	(7)				
	"				
	"				
	(3)				
	:				

	:				
	-				
	(-6)				
	-				
	(5)				
	-				
(7)					
	-				
(8)					

		:			
		0.160 .	%75 :		-
		0.160 .	%90 :		-
		0.160 .	%75 :		-
		0.063 .	%90 :		-
		0.160 .	%90 :		-

isobutylidene diurea crotonylidene diurea		2-1-
( )		

(172)   (39)

crotonylidene ( ) isobutylidene diurea diurea	:	

(+   +   ) %20 :   -
           :   -
(5)   1/4   %5
     (7)   3/5   .(7)   (6)
%5
%5
	:( )	

			6 5 4		
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1

(1)	(1)	(1)		(1)	(1)
		(2)			(2)
" " (2)		(2)		(2)	(3)
%2		%1 (4)			
		( )			(4)
(3)				(3)	(5)
	:(3) (2) (1)	(3)			crotonylidene diurea
	-	(7) (5)			(6)
		.( )			isobutylidene diurea
		(7)			(7)
	%2				
	(2)	(8)			
	-	(9)			(8)
	%2				
	(3)				(9)
	((1))				
	%2				
	1				
	(3) (2)				
	1				

		1-2-
	:	
(‏ + ‏) %18 : ‏ -	:( )	
%5 ‏ %3 : ‏ -		

	6 5 4				
K₂O	P₂O₅	N	K₂O	P₂O₅	N
6	5	4	3	2	1
	(1)	(1)		(1)	(1)
		(2)			(2)
		(2)		(2)	(3)
		%1 (4)			(4)
	:(3) (2) (1)	( )		(3)	(5)
	-				
	%2			(4)	
	(2)				
	-			(5)	
	%2				
	(3)			(-6)	

$$K_2O \quad P_2O_5 \quad N$$

(172) (42)

((1)　　)			%75	
%2			%2	
1			(　-6)	
1　　(3)　(2)			%2	
(　-2)			(7)	
			%75	
(3)　(1)			(8)	
(4)			%55	
:			%2	
%2　　-				
(4)				
%5　　-				
(3)				
%2.5　-				
(1)				
"　　　"				
"　　　"				
(　-2)				
3　　(3)				

	(-2)				
	(7) (1)				
	.				
	:				
	%2 -				
	%5 -(1)				
	(7)				
	"				
	"				
	(3)				
	:				
	:				
	(-6) -				
	(5) -				
	-				
	(7)				

	-			
	(8)			

	:			
-	%75 :		0.160 .	
-	%90 :		0.160 .	
-	%75 :		0.160 .	
-	%90 :		0.063 .	
-	%90 :		0.160 .	

يوريا أو crotonylidene diurea أو isobutylidene diurea فورمالدهايد (حسب ما هو ملائم)		
:		2-2-
crotonylidene diurea أو isobutylidene diurea أو يوريا فورمالدهايد (حسب ما هو ملائم)		
- %18 : (+)	( ) :	
- :		
%5 1/4		
(5) (6) (7). 3/5 (7)		
%5		

	6 5 4

K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1
	(1) :(3) (2) (1) - %2 (2) - %2 (3) ((1)) %2 (3) (2) 1	(1) (2) (2) %1 (4) ( ) (3) (7) (5) .( ) (7) (8) (9)		(1) (2) (3)	(1) (2) (3) (4) (5) crotonylidene diurea (6) isobutylidene diurea (7) (8) (9)

3-

		1-3-
	:	

(+) %18 : -	:( )	
%5 %3 : -		

	6 5 4		

K₂O	P₂O₅	N	K₂O	P₂O₅	N
6	5	4	3	2	1

(1)		(1)			(1)
		(2)			(2)
" " (2)		(2)			(3)
%2		( ) %1 (3)			(4)
(3)					(5)

isobutylidene diurea crotonylidene diurea		
( )		2-3-
( ) isobutylidene diurea crotonylidene diurea	:	

(172) (47)

- : 18% (+) - : 5% 1/4 (5) (6) (7). 3/5 (7) 5%	:( )		

			4 5 6		
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1

<table>
<tr><td>(1)
(2)
(3)
(4)
(5) crotonylidene diurea
(6) isobutylidene diurea
(7)
(8)
(9)</td><td></td><td></td><td>(1)
(2)
(2) (5) 1% ( )
(3)
(7) ( ).
(7)
(8) (9)</td><td></td><td>(1)
(2) " "
2%
(3)</td></tr>
</table>

‑4

	:
‑ : 18% (+) ‑ : 5% 5%	( ):

			6 5 4		
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1
(1)	(1)			(1)	
" " (2)				(2)	
%2	:(3) (2) (1)			(3)	
(3)	-			(4)	
	%2			(5)	
	(2)				
	-			(-6)	
	%2			%75	
	(3)				
	((1))			%2	
				(-6)	
	%2			%2	
	1			(7)	
	1 (3) (2)			%75	
	(-2)				

(172)   (50)

			(8)	
(4) (3) (1)			%55	
:				
- %2			%2	
(4)				
- %5				
(3)				
- %2.5				
(1)				
" "				
" "				
(-2)				
3 (3)				
(-2)				
(7) (1)				
.				
:				
- %2				

	(1)		
	– %5		
	(7)		
	"		
	"		
	(3)		
	:		
	:		
(-6)	–		
(5)	–		
	–		
	(7)		
	–		
	(8)		
		:	
		%75 : 0.160 .	–
		%90 : 0.160 .	–
		%75 : 0.160 .	–
		%90 :	–

(172)   (52)

		0.063 .
		- %90 :
		0.160 .

.

1 –

:

(1)
(2)
(3)
-                              - (   )   (4)
(5)
-                        -   (6)

6	5	4	3	2	1
		%15			1
%1					
/					
/					
%0.2					
" "		:			
		0.026 ×			

6	5	4	3	2	1
%0.2 " "		%26 %0.5			2
(5) : - -	:( ) (1) (2) (3)	%8 %1			3
		%6 %9 : 4			4

6	5	4	3	2	1
(5)	: (1) (2) (3)	%8 %1 %14			5
:%1 - - -		%18)　　: × (　　+ 0.026	1- 5　( )3　()3		6

6	5	4	3	2	1
		%18			7
:%1					
-		3/5			
-			1- 5 ( )3 ()3		
-					
		) : × (+ 0.026			

2-

:		
:	:	1-2-
(+ +) %15 : -		
%3 %3 %2 : -	:( )	
0.026 × : -		

(172)   (57)

			6 5 4		
K$_2$O	P$_2$O$_5$	N	K$_2$O	P$_2$O$_5$	N
6	5	4	3	2	1
(1) " (2) " %2 (3)		(1) (2) (4) (2) ( ) %1 (3) " %0.2 "			(1) (2) (3) (4)

( )	:	
(+ +) %20 : – %4 %4 %3 : – 0.026 × : –	:( )	2-2-

			6　5　4		
K$_2$O	P$_2$O$_5$	N	K$_2$O	P$_2$O$_5$	N
6	5	4	3	2	1
(1)　　　　　 "　　　　(2) 　　　　　" 　%2 　　　　(3)	(1) (2)　　　　%2 (2) (3)　　　　%2	(1) (2) (4)　(2) (　　)　%1 (3) %0.2 　　" 　　　"		(1) (2) (3)	(1) (2) (3) (4)

		3-2-
	:	

(+) %18 :	–		
%5 %3 :	–	:( )	
0.026 × :	–		

			6 5 4		
K$_2$O	P$_2$O$_5$	N	K$_2$O	P$_2$O$_5$	N
6	5	4	3	2	1
		(1) (2) (4) (2) ( ) %1 (3) " %0.2 "			(1) (2) (3) (4)

( )	:	4-2-

(172)   (60)

		(+) %18 :	-		
	%5 %3 :		-	:( )	
0.026 × :			-		

			6　5　4		
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1
	(1)	(1)		(1)	(1)
	(2) %2	(2)			(2)
	(2)	(2) (2)		(2)	(3)
	(3) %2	%1 (4)			
		( )		(3)	(4)
		(3)			
		%0.2			
		" "			

		5-2-

	:	
(+) %15 : -		
%5 %3 : -	:( )	
0.026 × : -		

			6 5 4		
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1
(1)		(1)			(1)
		(2)			(2)
" (2)		(2)			(3)
"		%1 (4)			
%2		( )			(4)
(3)		(3)			
		%0.2			
		"			
		"			

(172)   (62)

( )	:
(+) %15 : -	
%5 %3 : -	:( )
0.026 × : -	

	6 5 4		

K$_2$O	P$_2$O$_5$	N	K$_2$O	P$_2$O$_5$	N
6	5	4	3	2	1
(1)		(1)			(1)
		(2)			(2)
" (2)		(4) (2)			(3)
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	6 5 4				
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1
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%2 (3)					

		8-2-

( )	:	
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	6 5 4				
K_2O	P_2O_5	N	K_2O	P_2O_5	N
6	5	4	3	2	1
(1)	(1) %2			(1)	
" (2) " %2	(2) (2) %2			(2)	
(3)	(3)			(3)	

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-          -   (6)

6	5	4	3	2	1
		%25			1
:		%35			
		:			
		%80 -			
		2			
		%99 -			
		10			

6	5	4	3	2	1
:		%12			2
		%33.6 CaO %56			1-2
		%21 CaO %35			2-2
		%245)　　　%98 (			3
:		%24 %45			4

6	5	4	3	2	1
		%15 %28 -6) :(5-6) (3 %10 %17			5
:		%5 %10			(1)5
		%60 %99 : 0.063			(2)5
		%24	(2)5		(3)5

6	5	4	3	2	1
		%13 %3 :			6

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6	5	4	3	2	1
		%14			1( )
		%10			1( )

6	5	4	3	2	1
		7% 98% : 0.063			1( )
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-        -   (6)

6	5	4	3	2	1

6	5	4	3	2	1
		%19			( )2
		%2 8/10			( )2
%1 . . : .	: / (1) . (2) %1 . .	%2 ( )2 ( )2 .%40	( )2 ( )2 ( )2 /		( )2

6	5	4	3	2	1
		%2 %80 .	.		2( )

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6	5	4	3	2	1
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		0.063			
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6	5	4	3	2	1
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		%50 %98 : 0.063			( )3
		%17	( )3		( )3
		%5 %80 .	.		( )3

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6	5	4	3	2	1
		%12			4( )
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6	5	4	3	2	1
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6	5	4	3	2	1
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6	5	4	3	2	1
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%1	%1				
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		%35	( )6 ( )6		( )6

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		%70 %80 : 0.063			( )7

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6	5	4	3	2	1
Zn	:	%20	\ ( )7 \ ( )7		( )7
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0.2	0.2	(B)

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0.02	0.02	(Co)
0.1	0.5	(Cu)
0.3	2.0	(Fe)
0.1	0.5	(Mn)
-	0.02	(Mo)
0.1	0.5	(Zn)

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		=
0.01	0.1	(B)
-	0.002	(Co)
0.002	0.01	(Cu)
0.02	0.5	(Fe)
0.01	0.1	(Mn)
0.001	0.001	(Mo)
0.002	0.01	(Zn)

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0.01	(B)
0.002	(Co)
0.002	(Cu)
0.02	(Fe)
0.01	(Mn)
0.001	(Mo)
0.002	(Zn)

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(1) CAS				
60-00-4	$C_{10}H_{16}O_8N_2$	EDTA	Ethylenediaminetetraacetic acid	1

CAS [1]				
150-39-0	$C_{10}H_{18}O_7N_2$	HEEDTA	2-hydroxyethylethylenediaminetriacetic acid	2
67-43-6	$C_{14}H_{23}O_{10}N_3$	DTPA	diethylenetriaminepentaacetic acid	3
1170-02-1	$C_{18}H_{20}O_6N_2$	[o,o] EDDHA	ethylenediamine- N,N'-di[(ortho- hydroxyphenyl)acetic acid]	4
475475-49-1	$C_{18}H_{20}O_6N_2$	[o,p] EDDHA	ethylenediamine- N-[(ortho- hydroxyphenyl)acetic acid]- N'-[(para-hydroxyphenyl)acetic acid]	5
641632-90-8	$C_{20}H_{24}O_6N_2$	[o,o] EDDHMA	ethylenediamine- N,N'-di[(ortho- hydroxy-methylphenyl)acetic acid]	6
641633-41-2	$C_{20}H_{24}O_6N_2$	[o,p] EDDHMA	ethylenediamine- N-[(ortho-hydroxy- methylphenyl)acetic acid]- N'-[(para- hydroxy-methylphenyl)acetic acid]	7
85120-53-2	$C_{20}H_{20}O_{10}N_2$	EDDCHA	ethylenediamine- N,N'-di[(5-carboxy-2- hydroxyphenyl)acetic acid	8
57368-07-7 and 642045-40-7	$C_{18}H_{20}O_{12}N_2S_2$ + $n*(C_{12}H_{14}O_8N_2S)$	EDDCHA	ethylenediamine- N,N'-di[(2-hydroxy-5- sulfophenyl)acetic acid] and its condensation products	9
131669-35-7	$C_8H_{11}O_8N$	IDHA	Iminodisuccinic acid	10
35998-29-9	$C_{20}H_{24}N_2O_6$	HBED	N,N'-di(2-hydroxybenzyl)ethylenediamine- N,N'-diacetic acid	11

2-3-

Cu و Fe lignosulfonate و Zn lignosulfonate /

. Mn lignosulfonate و lignosulfonate

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CAS [1]				
8062-15-5	No chemical formula available	LS	Lignosulfonic acid	1
.				(1)

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4	**3**	**2**	**1**	

	4	3	2	1	
			2.25 4.5	Dicyandiamide ELINCS No 207-312-8	1
DCD 1 10 TZ			2.0 4.0	1,2,4-triazole (TZ) EC# EINECS No 207-312-8 EC# dicyandiamide (DCD) EINECS No 206-022-9	2
MP TZ 1 2			0.2 1.0	3-methylpyrazole (MP) EC# EINECS No 206-022-9 EC# 1,2,4-triazole (TZ) EINECS No 215-925-7	3

2-

	4	3	2	1	
	4	3	2	1	

4	3	2	1	
		0.09 0.2	N-(n-butyl) thiophosphoric triamide (NBPT) ELINCS No 435-740-7	1
		0.04 0.15	N-(2-nitrophenyl)phosphoric triamide (2-NPT) EC# EINECS No 477-690-9	2

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1.1	N
1.1	P_2O_5
1.1	K_2O

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25° إلى 50° وتطابق مع التعليمات في الجزء (2) من القسم (3) في هذا
الملحق يجب أن لا يتجاوز 4% (من الكتلة).

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Method 1		1
Method 2		2
Method 3		3
Method 4		4
Method 5		5
Method 6	( )	6
Method 7		7

Method 1
Methods for the application of thermal cycles

1- **Scope and field of application**

This document defines the procedures for the application of thermal cycles prior to the execution of the oil retention test for straight ammonium nitrate fertilisers of high nitrogen content and of the test on the resistance to detonation for both, straight and compound ammonium nitrate fertiliser of high nitrogen content.

The methods of the closed thermal cycles as described in this section are regarded as simulating sufficiently the conditions to be taken into account within the scope of application of title II, chapter IV, however, these methods may not necessarily simulate all conditions arising during transport and storage;

2- **Thermal cycles referred to in Annex III-1**

2-1 Field of application

This procedure is for thermal cycling prior to determining the oil retention of the fertiliser.

2-2   Principle and definition

In an Erlenmeyer flask, heat the sample from ambient temperature to 50 °C and maintain at this temperature for a period of two hours (phase at 50 °C). Thereupon cool the sample until a temperature of 25 °C is achieved and maintain at that temperature for two hours (phase at 25 °C). The combination of the successive phases at 50 °C and 25 °C forms one thermal cycle. After being subjected to two thermal cycles, the test sample is held at a temperature of 20 ±3 °C for the determination of the oil retention value.

2-3   Apparatus

Normal laboratory apparatus, in particular:

—   water baths thermostated at 25 (± 1) and 50 (± 1) °C respectively,
—   Erlenmeyer flasks with an individual capacity of 150 ml.

2-4   Procedure

Put each test sample of 70 (± 5) grams into an Erlenmeyer flask which is then sealed with a stopper.

Move each flask every two hours from the 50 °C bath to the 25 °C bath and vice versa.

Maintain the water in each bath at constant temperature and keep in motion by rapid stirring to ensure the water level comes above the level of the sample. Protect the stopper from condensation by a foam rubber cap.

3-   Thermal cycles to be used for Annex III-2

3-1   Field of application

This procedure is for thermal cycling prior to the execution of the detonability test.

3-2   Principle and definition

In a watertight box heat the sample from ambient temperature to 50 °C and maintain at this temperature for a period of one hour (phase at 50 °C). Thereupon cool the sample until a temperature of 25 °C is achieved and maintain at that temperature for one hour (phase at 25 °C). The combination of the successive phases at 50 °C and 25 °C forms one thermal cycle. After being subjected to the required number of thermal cycles, the test sample is held at a temperature of 20 ±3 °C pending the execution of the detonability test.

3-3   Apparatus

—   A water bath, thermostated in a temperature range of 20 to 51 °C with a minimum heating and cooling rate of 10 °C/h, or two water baths, one thermostated at a temperature of 20 °C, the other at 51 °C. The water in the bath(s) is continuously stirred; the volume of the bath should be large enough to guarantee ample circulation of the water.
—   A stainless steel box, watertight all around and provided with a thermocouple in the centre. The outside width of the box is 45 (± 2) mm and the wall thickness is 1,5 mm (see Figure 1). The height and length of the box can be chosen to suit the dimensions of the water bath, e.g. length 600 mm, height 400 mm.

3-4   Procedure

Place a quantity of fertilisers sufficient for a single detonation into the box and close the cover. Place the box in the water bath. Heat the water to 51 °C and measure the temperature in the centre of the fertiliser. One hour after the temperature at the centre has reached 50 °C cool the water. One hour after the temperature at the centre has reached 25 °C heat the water to start the second cycle. In the case of two water baths, transfer the box to the other bath after each heating/cooling period.

Figure 1

Method 2
Determination of oil retention

1-   Scope and field of application

This document defines the procedure for the determination of oil retention of straight ammonium nitrate fertilisers of high nitrogen content.

The method is applicable to both prilled and granular fertilisers which do not contain oil-soluble materials.

2-   Definition

Oil retention of a fertiliser: the quantity of oil retained by the fertilizer determined under the operating conditions specified, and expressed as a percentage by mass.

3-   Principle

Total immersion of the test portion in gas oil for a specified period, followed by the draining away of surplus oil under specified conditions. Measurement of the increase in mass of the test portion.

4-   Reagent

Gas oil

Viscosity max.: 5 mPas at 40 °C

Density: 0,8 to 0,85 g/ml at 20 °C

Sulphur content: ≤ 1,0 % (m/m)

Ash: ≤ 0,1 % (m/m)

5-   Apparatus

Ordinary laboratory apparatus, and:

5-1   Balance, capable of weighing to the nearest 0,01 gram.

5-2   Beakers, of capacity 500 ml.

5-3   Funnel, of plastic materials, preferably with a cylindrical wall at the upper end, diameter approximately 200 mm.

5-4   Test sieve, aperture 0,5 mm, fitting into the funnel (5-3).

Note*:* The size of the funnel and sieve is such as to ensure that only a few granules lie one above another and the oil is able to drain easily.

5-5   Filter paper, rapid filtering grade, creped, soft, mass 150 g/m2.

5-6   Absorbent tissue (laboratory grade).

6- Procedure

6-1   Two individual determinations are carried out in quick succession on separate portions of the same test sample.

6-2   Remove particles smaller than 0,5 mm using the test sieve (5-4). Weigh to the nearest 0,01 gram approximately 50 grams of the sample into the beaker (5-2). Add sufficient gas oil (section 4) to cover the prills or granules completely and stir carefully to ensure that the surfaces of all the prills or granules are fully wetted. Cover the beaker with a watch glass and leave to stand for one hour at 25 ($\pm$ 2) °C.

6-3   Filter the entire contents of the beaker through the funnel (5-3) containing the test sieve (5.4). Allow the portion retained by the sieve to remain there for one hour so that most of the excess oil can drain away.

6-4   Lay two sheets of filter paper (5.5) (about 500 × 500 mm) on top of each other on a smooth surface; fold the four edges of both filter papers upwards to a width of about 40 mm to prevent the prills from rolling away. Place two layers of absorbent tissue (5.6) in the centre of the filter papers. Pour the entire contents of the sieve (5.4) over the absorbent tissues and spread the prills evenly with a soft, flat brush. After two minutes lift one side of the tissues to transfer the prills to the filter papers beneath and spread them evenly over these with the brush. Lay another sheet of filter paper, similarly with its edges turned upward, on the sample and roll the prills between the filter papers with circular movements while exerting a little pressure. Pause after every eight circular movements to lift the opposite edges of the filter papers and return to the centre the prills that have rolled to the periphery. Keep to the following procedure: make four complete circular movements, first clockwise and then anticlockwise. Then roll the prills back to the centre as described above. This procedure to be carried out three times (24 circular movements, edges lifted twice). Carefully insert a new sheet of filter paper between the bottom sheet and the one above it and allow the prills to roll onto the new sheet by lifting the edges of the upper sheet. Cover the prills with a new sheet of filter paper and repeat the same procedure as described above. Immediately after rolling, pour the prills into a tared dish and reweigh to the nearest 0,01 gram to determine the mass of the quantity of gas oil retained.

6-5   Repeating the rolling procedure and reweighing

If the quantity of gas oil retained in the portion is found to be greater than 2 grams, place the portion on a fresh set of filter papers and repeat the rolling procedure, lifting the corners in accordance with section 6.4 (two times eight circular movements, lifting once). Then reweigh the portion.

7- Expression of the results

7-1   Method of calculation and formula

The oil retention, from each determination (6.1) expressed as a percentage by mass of the sieved test portion, is given by the equation:

$$\text{Oil retention } = \frac{m_2 - m_1}{m_1} \times 100$$

where:

m_1 is the mass, in grams, of the sieved test portion (6-2),

m_2 is the mass, in grams, of the test portion according to section 6-4 or 6-5 respectively as the result of the last weighing.

Take as the result the arithmetic mean of the two individual determinations.

Method 3
Determination of the combustible ingredients

1-   Scope and field of application

This document defines the procedure for the determination of the combustible content of straight ammonium nitrate fertilisers of high nitrogen content.

2-   Principle

The carbon dioxide produced by inorganic fillers is removed in advance with an acid. The organic compounds are oxidised by means of a chromic acid/sulphuric acid mixture. Carbon dioxide formed is absorbed in a barium hydroxide solution. The precipitate is dissolved in a solution of hydrochloric acid and measured by back-titration with sodium hydroxide solution.

3-   Reagents

3-1   Analytical-grade chromium (VI) trioxide Cr_2O_3;

3-2   Sulphuric acid, 60 % by volume: pour 360 ml of water into a one-litre beaker and carefully add 640 ml of sulphuric acid (density at 20 °C = 1.83 g/ml).

3-3   Silver nitrate: 0,1 mol/l solution.

3-4   Barium hydroxide

Weigh out 15 grams of barium hydroxide [$Ba(OH)_2. 8H_2O$], and dissolve completely in hot water. Allow to cool and transfer to a one-litre flask. Fill up to the mark and mix. Filter through a pleated filter paper.

3-5   Hydrochloric acid: 0,1 mol/l standard solution.

3-6   Sodium hydroxide: 0,1 mol/l standard solution.

3-7   Bromophenol blue: solution of 0,4 grams per litre in water.

3-8   Phenolphthalein: solution of 2 grams per litre in 60 % by volume ethanol.

3-9   Soda lime: particle dimensions, about 1,0 to 1,5 mm.

3-10   Demineralised water, freshly boiled to remove carbon dioxide.

4-   Apparatus

4-1   Standard laboratory equipment, in particular:

—   filter crucible with a plate of sintered glass and a capacity of 15 ml; plate diameter: 20 mm; total height: 50 mm; porosity 4 (pore diameter from 5 to 15 μm),

—   600-ml beaker.

4-2   Compressed nitrogen supply.

4-3   Apparatus made up of the following parts and assembled, if possible, by means of spherical ground joints (see Figure 2).

4-3-1   Absorption tube A about 200 mm long and 30 mm in diameter filled with soda lime (3-9) kept in place by fibreglass plugs.

4-3-2   500-ml reaction flask B with side arm and a round bottom.

4-3-3   Vigreux fractionating column about 150 mm long (C').

4-3-4   Double-surface condenser C, 200 mm long.

4-3-5   Dreschel bottle D acting as a trap for any excess of acid which may distil over.

4-3-6   Ice bath E to cool the Drechsel bottle.

4-3-7   Two absorption vessels F1 and F2, 32 to 35 mm in diameter, the gas distributor of which comprises a 10 mm disc of low-porosity sintered glass.

4-3-8   Suction pump and suction regulating device G comprising a T-shaped glass piece inserted into the circuit, the free arm of which is connected to the fine capillary tube by a short rubber tube fitted with a screw clamp.

Caution: The use of boiling chromic acid solution in an apparatus under reduced pressure is a hazardous operation and requires appropriate precautions.

5-   Procedure

5-1   Sample for analysis

Weigh approximately 10 grams of ammonium nitrate to the nearest 0,001 grams.

5-2   Removal of carbonates

Place the sample for analysis in the reaction flask B. Add 100 ml of H_2SO_4 (3-2). The prills or granules dissolve in about 10 minutes at ambient temperature. Assemble the apparatus as indicated in the diagram: connect one end of the absorption tube (A) to the nitrogen source (4-2) via a non-return flow device containing a pressure of 667 to 800 Pa and the other end to the feed tube which enters the reaction flask. Place the Vigreux fractionating column (C′) and the condenser (C) with cooling water supply in position. Adjust the nitrogen to provide a moderate flow through the solution, bring the solution to boiling point and heat for two minutes. At the end of this time there should be no more effervescence. If effervescence is seen, continue heating for 30 minutes. Allow solution to cool for at least 20 minutes with the nitrogen flowing through it.

Complete assembly of the apparatus as indicated in the diagram by connecting the condenser tube to the Drechsel bottle (D) and the bottle to the absorption vessels F1 and F2. The nitrogen must continue to pass through the solution during the assembly operation. Rapidly introduce 50 ml of barium hydroxide solution (3-4) into each of the absorption vessels (F1 and F2).

Bubble a stream of nitrogen through for about 10 minutes. The solution must remain clear in the absorbers. If this does not happen, the carbonate removal process must be repeated.

5-3   Oxidation and absorption

After withdrawing the nitrogen feed tube, rapidly introduce 20 grams of chromium trioxide (3-1) and 6 ml of silver nitrate solution (3-3) via the side arm of the reaction flask (B). Connect the apparatus to the suction pump and adjust the nitrogen flow so that a steady stream of gas bubbles passes through the sintered-glass absorbers F1 and F2.

Heat the reaction flask (B) until the liquid boils and keep it boiling for one and a half hours[1]. It may be necessary to adjust the suction-regulating valve (G) to control the nitrogen flow since it is possible that the barium carbonate precipitated during the test may block the sintered-glass discs. The operation is satisfactory when the barium hydroxide solution in the absorber F2 remains clear. Otherwise repeat the test. Stop heating and dismantle the apparatus. Wash each of the distributors (3-10) both inside and outside to remove barium hydroxide and collect the washings in the corresponding absorber. Place the distributors one after the other in a 600-ml beaker which will subsequently be used for the determination.

Rapidly filter under vacuum firstly the contents of absorber F2 and then of absorber F1 using the sintered-glass crucible. Collect the precipitate by rinsing the absorbers with water (3-10) and wash the crucible with 50 ml of the same water. Place the crucible in the 600- ml beaker and add about 100 ml of boiled water (3-10). Introduce 50 ml of boiled water into each of the absorbers and pass nitrogen through the distributors for five minutes. Combine the water with that from the beaker. Repeat the operation once to ensure that the distributors are rinsed thoroughly.

5-4   Measurement of the carbonates originating from organic material

---

[1]   A reaction time of one and a half hours, is sufficient in the case of most of the organic substances in the presence of silver nitrate catalyst

Add five drops of phenolphthalein (3-8) to the contents of the beaker. The solution becomes red in colour. Add hydrochloric acid (3-5) drop by drop until the pink colour just disappears. Stir the solution well in the crucible to check that the pink colour does not reappear. Add five drops of bromphenol blue (3-7) and titrate with hydrochloric acid (3-5) until the solution turns yellow. Add a further 10 ml of hydrochloric acid.

Heat the solution to boiling point and continue boiling for a maximum of one minute. Check carefully that no precipitate remains in the liquid.

Allow to cool and back titrate with the sodium hydroxide solution (3-6).

6-   Blank test

Carry out a blank test following the same procedure and using the same quantities of all reagents.

7-   Expression of the results

The content of combustible ingredients (C), expressed as carbon, as a percentage by mass of the sample, is given by the formula:

$$C\% = 0.06 \times \frac{V_1 - V_2}{E}$$

where:

E = the mass in grams of the test portion,

V_1 = the total volume in ml of 0,1 mol/l hydrochloric acid added after the change in colour of the phenolphthalein,

V_2 = the volume in ml of the 0,1 mol/l sodium hydroxide solution used for back titration.

Figure 2

A = Absorption tube filled with soda lime
B = Reaction flask
C = Vigreux fractionating column 150 mm long
C' = Double surface condenser 200 mm long
D = Drechsel bottle 250 ml
E = Ice bath
F₁ and F₂ = Absorption vessels 32 to 35 mm diameter assembled with spherical ground joints
     Gas distributor with 10 mm disc of low-porosity sintered glass
G = Suction-regulating device

to suction pump

Nitrogen supply

Method 4
Determination of the pH value

1-   Scope and field of application

This document defines the procedure for measuring the pH value of a solution of a straight ammonium nitrate fertiliser of high nitrogen content.

2-   Principle

Measurement of the pH of an ammonium nitrate solution by means of a pH meter.

3-   Reagents

Distilled or demineralised water, free from carbon dioxide.

(172)   (102)

3-1   Buffer solution, pH 6,88 at 20 °C

Dissolve $3,40 \pm 0,01$ grams of potassium dihydrogen orthophosphate (KH_2PO_4) in approximately 400 ml of water. Then dissolve $3,55 \pm 0,01$ grams of disodium hydrogen orthophosphate (Na_2HPO_4) in approximately 400 ml of water. Transfer the two solutions without loss into a 1 000-ml graduated flask, make up to the mark and mix.

Keep this solution in an airtight vessel.

3-2   Buffer solution, pH 4,00 at 20 °C

Dissolve $10,21 \pm 0,01$ grams of potassium hydrogen phthalate ($KHC_8O_4H_4$) in water, transfer without loss into a 1000-ml graduated flask, make up to the mark and mix.

Keep this solution in an airtight vessel.

3-3   Commercially available pH standard solutions may be used.

4-   **Apparatus**

pH meter, equipped with glass and calomel electrodes or equivalent, sensitivity 0,05 pH unit.

5-   **Procedure**

5-1   Calibration of the pH meter

Calibrate the pH meter (4) at a temperature of 20 ($\pm$ 1) °C, using the buffer solutions (3-1), (3-2) or (3-3). Pass a slow stream of nitrogen onto the surface of the solution and maintain this throughout the test.

5-2   Determination

Pour 100,0 ml of water onto 10 ($\pm$ 0,01) grams of the sample in a 250 ml beaker. Remove the insolubles by filtering, decanting or centrifuging the liquid. Measure the pH value of the clear solution at a temperature of 20 ($\pm$ 1) °C according to the same procedure as for the calibration of the meter.

6-   **Expression of the results**

Express the result in pH units, to the nearest 0,1 unit, and state the temperature used.

<div align="center">

Method 5

Determination of the particle size

</div>

1-   **Scope and field of application**

This document defines the procedure for the test sieving of straight ammonium nitrate fertilisers of high nitrogen content.

2-   **Principle**

The test sample is sieved on a nest of three sieves, either by hand or by mechanical means. The mass retained on each sieve is recorded and the percentage of material passing the required sieves are calculated.

3-   **Apparatus**

3-1   200-mm-diameter woven-wire test sieves with apertures of 2,0 mm, 1,0 mm and 0,5 mm respectively of standard ranges. One lid and one receiver for these sieves.

3-2   Balance to weigh to 0,1 gram.

3-3   Mechanical sieve shaker (if available) capable of imparting both vertical and horizontal motion to the test sample.

4-   **Procedure**

4-1   The sample is divided representatively into portions of approximately 100 grams.

4-2   Weigh one of these portions to the nearest 0,1 gram.

4-3   Arrange the nest of sieves in ascending order; receiver, 0,5 mm, 1 mm, 2 mm and place the weighed test portion on the top sieve. Fit the lid to the top of the nest of sieves.

4-4   Shake by hand or machine, imparting both a vertical and horizontal motion and if by hand, tapping occasionally. Continue this process for 10 minutes or until the quantity passing through each sieve in one minute is less than 0,1 gram.

4-5 Remove the sieves from the nest in turn and collect the material retained, brush gently from the reverse side with a soft brush, if necessary.

4-6 Weigh the material retained on each sieve and that collected in the receiver, to the nearest 0,1 gram.

5- Evaluation of the results

5-1 Convert the fraction masses to a percentage of the total of the fraction masses (not of the original charge).

Calculate the percentage in the receiver (i.e. < 0,5 mm): A %

Calculate the percentage retained on the 0,5 mm sieve: B %

Calculate the percentage passing 1,0 mm, i.e. (A + B) %

The sum of the fraction masses should be within 2% of the initial mass taken.

5-2 At least two separate analyses should be carried out and the individual results for A should not differ by more than 1,0 % absolute and for B by more than 1,5 % absolute. Repeat the test if this is not the case.

6- Expression of the results

Report the mean of the two values obtained for A on the one hand and for A + B on the other.

Method 6
Determination of the chlorine content (as chloride ion)

1- Scope and field of application

This document defines the procedure for the determination of the chlorine content (as chloride ion) of straight ammonium nitrate fertilizers with a high nitrogen content.

2- Principle

Chloride ions dissolved in water are determined by potentiometric titration with silver nitrate in an acidic medium.

3- Reagents

Distilled or demineralised water, free from chloride ions.

3-1 Acetone AR.

3-2 Concentrated nitric acid (density at 20 °C = 1,40 g/ml)

3-3 Silver nitrate 0,1 mol/l standard solution. Store this solution in a brown glass bottle.

3-4 Silver nitrate 0,004 mol/l standard solution - prepare this solution at the time of use.

3-5 Potassium chloride 0,1 mol/l standard reference solution. Weigh, to the nearest 0,1 mg, 3,7276 grams of analytical-grade potassium chloride, previously dried for one hour in an oven at 130 °C and cooled in a desiccator to ambient temperature. Dissolve in a little water, transfer the solution without loss into a 500-ml standard flask, dilute to the mark and mix.

3-6 Potassium chloride, 0,004 mol/l standard reference solution — prepare this solution at the time of use.

4- Apparatus

4-1 Potentiometer with silver indicating electrode and calomel reference electrode, sensitivity 2 mV, covering the range - 500 to + 500 mV.

4-2 Bridge, containing a saturated potassium nitrate solution, connected to the calomel electrode (4-1), fitted at the ends with porous plugs.

4-3 Magnetic stirrer, with a Teflon-coated rod.

4-4 Microburette with fine-pointed tip, graduated in 0,01 ml divisions.

5- Procedure

5-1 Standardisation of the silver nitrate solution

Take 5,00 ml and 10,00 ml of the standard reference potassium chloride solution (3-6) and place in two low-form beakers of convenient capacity (for example 250 ml). Carry out the following titration of the contents of each beaker.

Add 5 ml of the nitric acid solution (3-2), 120 ml of the acetone (3-1) and sufficient water to bring the total volume to about 150 ml. Place the rod of the magnetic stirrer

(4-3) in the beaker and set the stirrer in motion. Immerse the silver electrode (4-1) and the free end of the bridge (4-2) in the solution. Connect the electrodes to the potentiometer (4-1) and, after verifying the zero of the apparatus, note the value of the starting potential.

Titrate, using the microburette (4-4), adding initially 4 or 9 ml respectively of the silver nitrate solution corresponding to the standard reference potassium chloride solution used. Continue the addition in 0,1 ml portions for the 0,004 mol/l solutions and in 0,05 ml portions for the 0,1 mol/l solutions. After each addition, await the stabilization of the potential.

Record the volumes added and the corresponding values of the potential in the first two columns of a table.

In a third column of the table, record the successive increments ($\Delta_1 E$) of the potential E. In a fourth column, record the differences ($\Delta_2 E$) positive or negative, between the potential increments ($\Delta_1 E$). The end of the titration corresponds to the addition of the 0,1 or 0,05 ml portion (V_1) of the silver nitrate solution which gives the maximum value of $\Delta_1 E$.

In order to calculate the exact volume (V_{eq}) of the silver nitrate solution corresponding to the end of the reaction, use the formula:

$$Veq = V0 + (V1 \times \frac{b}{B})$$

where:

V_0 is the total volume, in ml, of the silver nitrate solution immediately lower than the volume which gives the maximum increment of $\Delta_1 E$,

V_1 is the volume, in ml, of the last portion of the silver nitrate solution added (0,1 or 0,05 ml),

b is the last positive value of $\Delta_2 E$,

B is the sum of the absolute values of the last positive values of $\Delta_2 E$ and the first negative value of $\Delta_2 E$ (see example in Table 1).

5-2 Blank test

Carry out a blank test and take account thereof when calculating the final result.

The result V_4 of the blank test on the reagents is given, in ml, by the formula:

$$V4 = 2V3 - V2$$

where:

V_2 is the value, in ml, of the exact volume (V_{eq}) of the silver nitrate solution corresponding to the titration of 10 ml of the potassium chloride standard reference solution used,

V_3 is the value, in ml, of the exact volume (V_{eq}) of the silver nitrate solution corresponding to the titration of 5 ml of the potassium chloride standard reference solution used.

5-3 Check test

The blank test can at the same time serve as a check that the apparatus is functioning satisfactorily and that the test procedure is being implemented correctly.

5-4 Determination

Take a portion of sample in the range 10 to 20 grams and weigh to the nearest 0,01 gram. Transfer quantitatively to a 250-ml beaker. Add 20 ml of water, 5 ml of nitric acid solution (3-2), 120 ml of acetone (3-1) and sufficient water to bring the total volume to about 150 ml.

Place the rod of the magnetic stirrer (4-3) in the beaker, place the beaker on the stirrer and set the stirrer in motion. Immerse the silver electrode (4-1) and the free end of the bridge (4-2) in the solution, connect the electrodes to the potentiometer (4-1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Titrate with the silver nitrate solution, by additions from the microburette (4-4) in increments of 0,1 ml. After each addition, await the stabilisation of the potential.

Continue the titration as specified in 5-1, starting from the fourth paragraph: 'Record the volumes added and the corresponding values of the potential in the first two columns of a table …'.

6- Expression of the results

Express the result of the analysis as the percentage of chlorine contained in the sample as received for analysis. Calculate the percentage of chlorine (Cl) content from the formula:

$$Cl\% = \frac{0.3545 \times T \times (V5 - V4) \times 100}{m}$$

where:

T is the concentration of silver nitrate solution used, in mol/l

V_4 is the result, in ml, of the blank test (5-2),

V_5 is the value, in ml, of V_{eq} corresponding to the determination (5-4),

m is the mass, in grams, of the test portion.

Table 1: Example

Volume of the silver nitrate solution V (ml)	Potential E (mV)	$\Delta_1 E$	$\Delta_2 E$
4,80	176		
4,90	211	35	+ 37
5,00	283	72	− 49
5,10	306	23	− 10
5,20	319	13	

$$V_{eq} = 4,9 + 0,1 \times \frac{37}{37 + 49} = 4,943$$

Method 7

Determination of copper

1- Scope and field of application

This document defines the procedure for the determination of copper content of straight ammonium nitrate fertilisers of high nitrogen content.

2- Principle

The sample is dissolved in dilute hydrochloric acid and the copper is determined by atomic absorption spectrophotometry.

3- Reagents

3-1 Hydrochloric acid (density at 20 °C = 1,18 g/ml).

3-2 Hydrochloric acid, 6 mol/l solution.

3-3 Hydrochloric acid 0,5 mol/l solution.

3-4 Ammonium nitrate.

3-5 Hydrogen peroxide, 30 % w/v

3-6   Copper solution[1](stock): weigh, to the nearest 0,001 gram, 1 gram of pure copper, dissolve in 25 ml 6 mol/l hydrochloric acid solution (3-2), add 5 ml of hydrogen peroxide (3-5) in portions and dilute to 1 litre with water. 1 ml of this solution contains 1 000 µg of copper (Cu).

    3-6-1   Copper solution (dilute): dilute 10 ml of stock solution (3-6) to 100 ml with water and then dilute 10 ml of the resulting solution, to 100 ml with water, 1 ml of the final dilution contains 10 µg of copper (Cu).
Prepare this solution at the time of use.

4-   Apparatus

Atomic absorption spectrophotometer with a copper lamp (324,8 nm).

5-   Procedure

5-1   Preparation of the solution for analysis

Weigh, to the nearest 0,001 gram, 25 grams of the sample, place it in a 400-ml beaker, add carefully 20 ml of hydrochloric acid (3-1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid, if necessary. When effervescence has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15 ml 6 mol/l hydrochloric acid solution (3-2) and 120 ml of water. Stir with the glass rod, which should be left in the beaker, and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete and then cool.

Transfer the solution quantitatively into a 250-ml graduated flask, by washing the beaker with 5 ml 6 mol/l hydrochloric acid (3-2), and twice with 5 ml of boiling water, make up to the mark with 0,5 mol/l hydrochloric acid (3-3) and mix carefully.

Filter through a copper-free filter paper[1], discarding the first 50 ml.

5-2   Blank solution

Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final results.

5-3   Determination

    5-3-1   Preparation of sample and blank test solutions

Dilute the sample solution (5-1) and the blank test solution (5-2) with 0,5 mol/l hydrochloric acid solution (3-3) to a concentration of copper within the optimal measuring range of the spectrophotometer. Normally no dilution is needed.

    5-3-2   Preparation of the calibration solutions

By diluting the standard solution (3-6-1) with 0,5 mol/l hydrochloric acid solution (3-3), prepare at least five standard solutions corresponding to the optimal measuring range of the spectrophotometer (0 to 5,0 mg/l Cu). Before making up to the mark, add to every solution ammonium nitrate (3-4) to give concentration of 100 mg per ml.

5-4   Measurement

Set up the spectrophotometer (4) at a wavelength of 324,8 nm. Use an oxidising air-acetylene flame. Spray successively, in triplicate, the calibration solution (5-3-2), the sample solution and the blank solution (5-3-1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances of every standard used as the ordinates and the corresponding concentrations of copper in µg/ml as the abscissae.

Determine the concentration of copper in the final sample and blank solutions by reference to the calibration curve.

6-   Expression of the results

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(1)   Commercially available standard copper solution may be used
(1)   Whatman 541 or equivalent.

Calculate the copper content of the sample taking into account the mass of the test sample, the dilutions carried out in the course of the analysis and the value of the blank. Express the result as mg Cu/kg.

.4

4-   Determination of resistance to detonation

4-1   Scope and field of application

This document defines the procedure for the determination or resistance to detonation of ammonium nitrate fertilisers of high nitrogen content.

4-2   Principle

The test sample is confined in a steel tube and subjected to detonation shock from an explosive booster charge. Propagation of the detonation is determined from the degree of crushing of lead cylinders on which the tube rests horizontally during the test.

4-3   Materials

4-3-1   Plastic explosive containing 83 to 86 % penthrite
Density: 1 500 to 1 600 kg/m3
Detonation velocity: 7 300 to 7 700 m/s
Mass: 500 ($\pm$ 1) gram.

4-3-2   Seven lengths of flexible detonating cord with non-metallic sleeve
Filling mass: 11 to 13 g/m
Length of each cord: 400 ($\pm$ 2) mm.

4-3-3   Compressed pellet of secondary explosive, recessed to receive detonator
Explosive: hexogen/wax 95/5 or tetryl or similar secondary explosive, with or without added graphite.
Density: 1 500 to 1 600 kg/m3
Diameter: 19 to 21 mm
Height: 19 to 23 mm
Central recess to receive detonator: diameter 7 to 7,3 mm, depth 12 mm.

4-3-4   Seamless steel tube as specified in ISO 65 — 1981 — Heavy Series, with nominal dimensions DN 100 (4")
Outside diameter: 113,1 to 115,0 mm
Wall thickness: 5,0 to 6,5 mm
Length: 1 005 ($\pm$ 2) mm.

4-3-5   Bottom place
Material: steel of good weldable quality
Dimensions: 160 × 160 mm
Thickness: 5 to 6 mm

4-3-6   Six lead cylinders
Diameter: 50 ($\pm$ 1) mm
Height: 100 to 101 mm
Materials: soft lead, at least 99,5 % purity.

4-3-7   Steel block
Length: at least 1 000 mm
Width: at least 150 mm
Height: at least 150 mm
Mass: at least 300 kg if there is no firm base for the steel block.

4-3-8   Plastic or cardboard cylinder for booster charge
Wall thickness: 1,5 to 2,5 mm
Diameter: 92 to 96 mm
Height: 64 to 67 mm

4-3-9   Detonator (electric or non-electric) with initiation force 8 to 10

4-3-10   Wooden disc

Diameter: 92 to 96 mm. Diameter to be matched to the internal diameter of the plastic or cardboard cylinder (4-3-8)

Thickness: 20 mm

4-3-11   Wooden rod of same dimensions as detonator (4-3-9)

4-3-12   Dressmaking pins (maximum length 20 mm)

4-4   Procedure

4-4-1   Preparation of booster charge for insertion into steel tube

There are two methods of initiation of the explosive in the booster charge, depending on the availability of equipment.

4-4-1-1 Seven-point simultaneous initiation

The booster charge prepared for use is shown in Figure 1.

4-4-1-1-1   Drill holes in the wooden disc (4-3-10) parallel to the axis of the disc through the centre and through six points symmetrically distributed around a concentric circle 55 mm in diameter. The diameter of the holes must be 6 to 7 mm (see Section A-B in Figure 1), depending on the diameter of the detonating cord used (4-3-2).

4-4-1-1-2   Cut seven lengths of flexible detonating cord (4-3-2) each 400 mm long, avoiding any loss of explosive at each end by making a clean cut and immediately sealing the end with adhesive. Push each of the seven lengths through the seven holes in the wooden disc (4-3-10) until their ends project a few centimetres on the other side of the disc.

Then insert a small dressmaking pin (4-3-12) transversally into the textile sleeve of each length of cord 5 to 6 mm from the end and apply adhesive around the outside of the lengths of cord in a band 2 cm wide adjacent to the pin. Finally, pull the long piece of each cord to bring the pin into contact with the wooden disc.

4-4-1-1-3   Shape the plastic explosive (4-3-1) to form a cylinder 92 to 96 mm in diameter, depending on the diameter of the cylinder (4-3-8). Stand this cylinder upright on a level surface and insert the shaped explosive.

Then insert the wooden disc[1] carrying the seven lengths of detonating cord into the top of the cylinder and press it down onto the explosive. Adjust the height of the cylinder (64 to 67 mm) so that its top edge does not extend beyond the level of the wood. Finally, fix the cylinder to the wooden disc for instance with staples or small nails, around its entire circumference.

4-4-1-1-4   Group the free ends of the seven lengths of detonating cord around the circumference of the wooden rod (4-3-11) so that their ends are all level in a plane perpendicular to the rod. Secure

_____

[1]   The diameter of the disc must always correspond to the inside diameter of the cylinder.

them in a bundle around the rod by means of adhesive tape[2].

4-4-1-2   Central initiation by a compressed pellet

The booster charge prepared for use is shown in Figure 2.

    4-4-1-2-1   Preparing a compressed pellet

Taking the necessary safety precautions, place 10 grams of a secondary explosive (4-3-3) in a mould with an inside diameter of 19 to 21 mm and compress to the correct shape and density.

(The ratio of diameter: height should be roughly 1:1).

In the centre of the bottom of the mould there is a peg, 12 mm in height and 7,0 to 7,3 mm in diameter (depending on the diameter of the detonator used), which forms a cylindrical recess in the compressed cartridge for subsequent insertion of the detonator.

    4-4-1-2-2   Preparing the booster charge

Place the explosive (4-3-1) into the cylinder (4-3-8) standing upright on a level surface, then press it down with a wooden die to give the explosive a cylindrical shape with a central recess. Insert the compressed pellet into this recess. Cover the cylindrically shapedexplosive containing the compressed pellet with a wooden disc (4.3.10) having a central hole 7,0 to 7,3 mm in diameter for insertion of a detonator. Fix the wooden disc and the cylinder together with a cross of adhesive tape. Ensure that the hole drilled in the disc and the recess in the compressed pellet are coaxial by inserting the wooden rod (4-3-11).

4-4-2   Preparing steel tubes for the detonation tests

At one end of the steel tube (4-3-4), drill two diametrically opposed holes 4 mm in diameter perpendicularly through the side wall at a distance of 4 mm from the edge.

Butt weld the bottom plate (4-3-5) to the opposite end of the tube, completely filling the right angle between the bottom place and the wall of the tube with weld metal around the entire circumference of the tube.

4-4-3   Filling and charging the steel tube

See Figures 1 and 2.

    4-4-3-1   The test sample, the steel tube and the booster charge must be conditioned to temperatures of 20 (± 5) °C. 16 to 18 kg of the test sample are needed for two detonation tests.

    4-4-3-2   Place the tube upright with its square bottom place resting on a firm, flat surface, preferably concrete. Fill the tube to about one-third of its height with the test sample and drop it 10 cm vertically onto the floor five times to compact the prills or granules as densely as possible in the tube. To accelerate compaction, vibrate the tube by striking the side wall with a 750 to 1000-gram hammer between drops for a total of 10 times.

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(2)   *NB:* When the six peripheral lengths of cord are taut after assembly, the central cord must remain slightly slack.

Repeat this charging method with another portion of the test sample. Finally, a further addition shall be made such that, after compaction by raising and dropping the tube 10 times and a total of 20 intermittent hammer blows, the charge fills the tube to a distance of 70 mm from its orifice.

The filling height of the sample must be adjusted in the steel tube so that the booster charge (4-4-1-1 or 4-4-1-2) to be inserted later will be in close contact with the sample over its entire surface.

4-4-3-3   Insert the booster charge into the tube so that it is in contact with the sample; the top surface of the wooden disc must be 6 mm below the end of the tube. Ensure essential close contact between explosive and test sample by adding or removing small quantities of sample. As shown in Figures 1 and 2, split pins should be inserted through the holes near the open end of the tube and their legs opened flat against the tube.

4-4-4   Positioning of the steel tube and lead cylinders (see figure 3)

4-4-4-1   Number the bases of the lead cylinders (4-3-6) 1 to 6. Make six marks 150 mm apart on the centre line of a steel block (4-3-7) lying on a horizontal base, with the first mark at least 75 mm from the edge of the block. Place a lead cylinder upright on each of these marks, with the base of each cylinder centred on its mark.

4-4-4-2   Lay the steel tube prepared according to 4-4-3 horizontally on the lead cylinders so that the axis of the tube is parallel to the centre line of the steel block and the welded end of the tube extends 50 mm beyond lead cylinder No 6. To prevent the tube from rolling, insert smallwooden wedges between the tops of the lead cylinders and the tube wall (one on each side) or place a cross of wood between the tube and the steel block.

Note: Make sure that the tube is in contact with all six lead cylinders; a slight curvature of the tube surface can be compensated for by rotating the tube about its longitudinal axis; if any of the lead cylinders is too tall, tap the cylinder in question carefully with a hammer until it is the required height.

4-4-5   Preparation for detonation

4-4-5-1   Set up the apparatus according to the 4-4-4 in a bunker or suitably prepared underground site (e.g. mine or tunnel). Ensure that the temperature of the steel tube is kept at 20 ($\pm$ 5) °C before detonation.

Note: Should such firing sites not be available, the work can, if necessary, be done in a concrete lined pit covered over with wooden beams. Detonation can cause steel fragments to be projected with high kinetic energy, therefore, firing must be carried out at a suitable distance from dwellings or thoroughfares.

4-4-5-2   If the booster charge with seven-point initiation is used, ensure that the detonation cords are stretched out as described in the footnote to 4-4-1-1-4 and arranged as horizontally as possible.

4-4-5-3   Finally, remove the wooden rod and replace with the detonator. Do not carry out firing until the danger zone has been evacuated and the test personnel have taken cover.

4-4-5-4   Detonate the explosive.

4-4-6 Allow sufficient time for the fumes (gaseous and sometimes toxic decomposition products such as nitrous gases) to disperse, then collect the lead cylinders and measure their heights with a Vernier caliper

Record for each of the marked lead cylinders, the degree of crushing expressed as a percentage of the original height of 100 mm. If the cylinders are crushed obliquely, record the highest and the lowest values and calculate the average.

4-4-7 A probe for continuous measurement of the detonation velocity can be used; the probe should be inserted longitudinally to the axis of the tube or along its side wall

4-4-8 Two detonation tests per sample are to be carried out

4-5 Test report

Values for the following parameters are to be given in the test report for each of the detonation tests:

— the values actually measures for the outside diameter of the steel tube and for the wall thickness,
— the Brinell hardness of the steel tube,
— the temperature of the tube and the sample shortly before firing,
— the packing density (kg/m3) of the sample in the steel tube,
— the height of each lead cylinder after firing, specifying the corresponding cylinder number,
— method of initiation employed for the booster charge.

4-5-1 Evaluation of test results

If, in each firing, the crushing of at least one lead cylinder is less than 5 %, the test shall be considered conclusive and the sample in conformity with the requirements of Annex III.2.

Figure 1

Booster charge with seven-point initiation

Dimensions in mm

Section C – D

Section A – B

① Steel tube	⑥ Test sample
② Wooden disc with seven holes	⑦ 4-mm-diameter hole drilled to receive split pin ⑧
③ Plastic or cardboard cylinder	⑧ Split pin
④ Detonating cords	⑨ Wooden rod surrounded by ④
⑤ Plastic explosive	⑩ Adhesive tape for securing ④ around ⑨

Figure 3

Booster charge with central initiation

Dimensions in mm

①	Steel tube	⑥	Compressed pellet	
②	Wooden disc	⑦	Test sample	
③	Plastic or cardboard cylinder	⑧	4-mm-diameter hole drilled to receive split pin ⑨	
④	Wooden rod	⑨	Split pin	
⑤	Plastic explosive	⑩	Wooden die for ⑤	

Figure 3

Positioning of the steel tube on the firing site

A – B

① Steel tube
② Lead cylinders
③ Steel block
④ Bottom plate
⑤ Booster charge

Dimensions in mm

numbers of the
lead cylinders

1 to 6

(4)

رقم الطريقة	
A	
B	
Method 1	
Methods 2	
Method 2.1	
Methods 2.2	
Method 2.2.1	Ulsch
Method 2.2.2	Arnd
Method 2.2.3	Devarda
Method 2.3	
Method 2.3.1	
Method 2.3.2	
Method 2.3.3	
Method 2.4	
Method 2.5	
Methods 2.6	
Method 2.6.1	
Method 2.6.2	

رقم الطريقة	
Method 2.6.3	HPLC - Isobutylenediurea و crotonylidenediurea (طريقة أ)، وmethylen-urea oligomers (طريقة ب)
Methods 3	
Methods 3.1	
Method 3.1.1	
Method 3.1.2	%2 (20)
Method 3.1.3	%2 (20)
Method 3.1.4	
Methods 3.1.5	
Method 3.1.5.1	Petermann على 65°س
Method 3.1.5.2	Petermann على درجة الحرارة المحيطة
Method 3.1.5.3	Joulie's alkaline ammonium citrate
Method 3.1.6	
Method 3.2	(Gravimetric Method Using Quinoline Phosphomolybdate)
Method 4	
Method 4.1	
Method 5	
Method 5.1	- :
Method 6	
Method 6.1	

رقم الطريقة	
Methods 7	
Method 7.1	( )
Method 7.2	
Methods 8	
Method 8.1	
Method 8.2	
Method 8.3	) (
Method 8.4	
Method 8.5	
Method 8.6	oxalate
Method 8.7	
Method 8.8	complexometry
Method 8.9	
Method 8.10	
Methods 9	**%10**
Method 9.1	
Method 9.2	
Method 9.3	
Method 9.4	( )
رقم الطريقة	

رقم الطريقة	
Method 9.5	azomethine-H
Method 9.6	
Method 9.7	
Method 9.8	
Method 9.9	
Method 9.10	ammonium thiocyanate
Method 9.11	
Methods 10	**10%**
Method 10.1	
Method 10.2	
Method 10.3	
Method 10.4	( )
Method 10.5	
Method 10.6	1-nitroso-2-naphthol
Method 10.7	
Method 10.8	
Method 10.9	
Method 10.10	8-Hydroxyquinoline

رقم الطريقة	
Method 10.11	
Methods 11	
Method 11.1	
Method 11.2	EDTA وHEDTA وDTPA
Method 11.3	o,o EDDHA وo,o EDDHMA
Method 11.4	EDDHSA
Method 11.5	o,p EDDHA
Methods 12	
Method 12.1	dicyandiamide
Method 12.2	NBPT
Methods 13	
Method 13.1	

A. METHOD OF SAMPLING FOR THE CONTROL OF FERTILISERS

INTRODUCTION

Correct sampling is a difficult operation which requires the greatest of care. The need to obtain a sufficiently representative sample for the official testing of fertilisers cannot, therefore, be stressed too much.

The sampling method described below must be applied with strict accuracy by specialists with experience of the conventional sampling procedure.

1- Purpose and scope

Samples intended for the official control of fertilisers, for quality and composition, shall be taken according to the methods described below.

Samples thus obtained shall be considered as representative of the sampled portions.

2- Sampling officers

The samples shall be taken by specialist officers authorised for that purpose by the Member States.

3- Definitions

Sampled portion: A quantity of product constituting a unit, and having characteristics presumed to be uniform.

Incremental sample: A quantity taken from one point in the sampled portion.

Aggregate sample: An aggregate of incremental samples taken from the same sampled portion.

Reduced sample: A representative part of the aggregate sample, obtained from the latter by a process of reduction.

Final sample: A representative part of the reduced sample.

4-   **Apparatus**

4-1   The sampling apparatus must be made of materials which cannot affect the characteristics of the products to be sampled. Such apparatus may be officially approved by the Member States.

4-2   Apparatus recommended for the sampling of solid fertilisers

     4-2-1   Manual sampling

     4-2-1-1 Flat-bottomed shovel with vertical sides.

     4-2-1-2 Sampling spear with a long split or compartments. The dimensions of the sampling spear must be appropriate to the characteristics of the sampled portion (depth of container, dimensions of sack, etc.) and to the particle size of the fertiliser.

     4-2-2   Mechanical sampling

         Approved mechanical apparatus may be used for the sampling of moving fertilisers.

     4-2-3   Divider

         Apparatus designed to divide the sample into equal parts may be used for taking incremental samples and for the preparation of reduced and final samples.

4-3   Apparatus recommended for the sampling of fluid fertilisers

     4-3-1   Manual sampling

         Open tube, probe, bottle or another appropriate equipment able to take samples at random from the sampled portion.

     4-3-2   Mechanical sampling

         Approved mechanical apparatus may be used for sampling of moving fluid fertilisers.

5-   **Quantitative requirements**

5-1   Sampled portion

     The size of the sampled portion must be such that each of its constituent parts can be sampled.

5-2   Incremental samples

     5-2-1   Loose solid fertilisers or fluid fertilisers in containers exceeding 100 kg

         5-2-1-1 Sampled portions not exceeding 2,5 tonnes:

             Minimum number of incremental samples: seven

         5-2-1-2 Sampled portions exceeding 2,5 tonnes and up to 80 tonnes:

             Minimum number of incremental samples:

$$\sqrt{20 \text{ times the number of tonnes making up the sampled portion}} \;^{(1)}$$

         5-2-1-3 Sampled portions exceeding 80 tonnes:

             Minimum number of incremental samples: 40

     5-2-2   Packaged solid fertilisers or fluid fertilisers in containers (= packages each not exceeding 100 kg)

         5-2-2-1 Packages of more than 1 kg

             5-2-2-1-1   Sampled portions of less than five packages:

                 Minimum number of packages to be sampled[2]: all packages.

             5-2-2-1-2   Sampled portions of five to 16 packages:

---

(1)   Where the number obtained is a fraction, it should be rounded up to the next whole number.

(2)   For packages whose contents do not exceed 1 kg, an incremental sample shall be the contents of one original package.

Minimum number of packages to be sampled[2]: four.

5-2-2-1-3   Sampled portions of 17 to 400 packages:
Minimum number of packages to be sampled[2]:

$$\sqrt{\text{number of packages making up the sampled portion}}$$

[1]

5-2-2-1-4   Sampled portions exceeding 400 packages:
Minimum number of packages to be sampled[2]: 20.

5-2-2-2   Packages not exceeding 1 kg:
Minimum number of packages to be sampled[2]: four.

5-3   Aggregate sample

A single aggregate sample per sampled portion is required. The total mass of the incremental samples making up the aggregate sample shall be not less than the following:

5-3-1   Loose solid fertilisers or fluid fertilisers in containers exceeding 100 kg: 4 kg.

5-3-2   Packaged solid fertilisers or fluid fertilisers in containers (= packages) each not exceeding 100 kg

5-3-2-1   Packages of more than 1 kg: 4 kg

5-3-2-2   Packages not exceeding 1 kg: mass of the contents of four original packages.

5-3-3   Ammonium nitrate fertiliser sample for tests according to Annex III.2: 75 kg

5-4   Final samples

The aggregate sample gives the final samples on reduction when necessary. Analysis of at least one final sample is required. The mass of the sample for analysis shall not be less than 500 g.

5-4-1   Solid and fluid fertilisers

5-4-2   Ammonium nitrate fertiliser sample for tests

The aggregate sample gives the final sample for tests on reduction when necessary.

5-4-2-1   Minimum final sample mass for Annex III.1 tests: 1 kg

5-4-2-2   Minimum final sample mass for Annex III.2 tests: 25 kg

6-   Instructions for taking, preparing and packaging the samples

6-1   General

The samples must be taken and prepared as quickly as possible bearing in mind the precautions necessary to ensure that they remain representative of the fertiliser sampled. Instruments and also surfaces and containers intended to receive samples must be clean and dry.

In the case of fluid fertilisers, if possible the sampled portion should be mixed prior to sampling.

6-2   Incremental samples

Incremental samples must be taken at random throughout the whole sampled portion and they must be of approximately equal sizes.

6-2-1   Loose solid fertilisers or fluid fertilisers in containers exceeding 100 kg

An imaginary division shall be made of the sampled portion into a number of approximately equal parts. A number of parts corresponding to the number of incremental samples required in accordance with 5-2 shall be selected at random and at least one sample taken from each of these parts. Where it is not possible to comply with the requirements of 5-1 when sampling bulk fertilisers or fluid fertilisers in containers exceeding 100 kg the sampling should be carried out when the sampled portion is being

moved (loading or unloading). In this case samples shall be taken from the randomly selected notional parts as defined above while these are being moved.

6-2-2   Packaged solid fertilisers or fluid fertilisers in containers (= packages) each not exceeding 100 kg

Having selected the required number of packages for sampling as indicated in 5-2, part of the contents of each package shall be removed. Where necessary, the samples shall be taken after emptying the packages separately.

6-3   Preparation of aggregate sample

The incremental samples shall be mixed to form a single aggregate sample.

6-4   Preparation of the final sample

The material in the aggregate sample shall be carefully mixed[1].

If necessary the aggregate sample should first be reduced to at least 2 kg (reduced sample) either by using a mechanical divider or by the quartering method.

At least three final samples shall then be prepared, of approximately the same amount and conforming to the quantitative requirements of 5-4. Each sample shall be put into an appropriate air tight container.

All necessary precautions shall be taken to avoid any change in the characteristics of the sample.

For the tests of Annex III, sections 1 and 2, the final samples shall be kept at a temperature between 0 °C and 25 °C.

7-   Packaging of final samples

The containers or packages shall be scaled and labelled (the total label must be incorporated in the seal) in such a manner that they cannot be opened without damaging the seal.

8-   Sampling record

A record must be kept of each sampling, permitting each sampled portion to be identified unambiguously.

9-   Destination of samples

For each sample portion at least one final sample shall be sent as quickly as possible to an authorised analytical laboratory or to the test institution, together with the information necessary for the analysis or the test.

B. METHODS FOR THE ANALYSIS OF FERTILISERS

General observations

Laboratory equipment

In the descriptions of the methods, general laboratory equipment has not been precisely defined, except that the sizes of flasks and pipettes are given. In all cases laboratory apparatus must be well cleaned, particularly when small quantities of elements are to be determined.

Control tests

Before analysis it is necessary to ensure that all apparatus functions well and that the analytical technique is carried out correctly, using where appropriate chemical compounds of known composition (e.g. ammonium sulphate, mono potassium phosphate, etc.). Nevertheless, the results from analysed fertilisers can indicate wrong chemical composition if the analytical technique is not rigorously followed. On the other hand, a certain number of determinations are empirical and are relative to products of complex chemical composition. It is recommended that where available, laboratories should make use of standard reference fertilisers of well defined composition.

General provisions relating to methods of analysing fertilisers

1-   Reagents

Unless otherwise specified in the method of analysis, all of the reagents must be analysis-pur (a.p.). Where micro-nutrients are to be analysed the purity of the reagents must be checked by

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[1]   Any lumps shall be broken up (if necessary by separating them out and returning them to the sample).

means of a blank test. Depending upon the result obtained, it might be necessary to conduct a further purification.

2- Water

Where dissolution, dilution, rinsing or washing operations referred to in the methods of analysis do not specify the nature of solvents or diluents the use of water is implied. Normally, the water will have to be demineralised or distilled. In these specific instances, as mentioned in the method of analysis, that water will have to be subjected to specific purification processes.

3- Laboratory equipment

In view of the equipment normally used in inspection laboratories, the apparatus described in the methods of analysis is restricted to special instruments and apparatus or to such demanded by any specific requirements.

This equipment must be perfectly clean, above all where small quantities are to be determined. The laboratory will have to ensure the accuracy of any graduated glassware used by referring to appropriate metrological standards.

Method 1

Preparation of the sample for analysis

EN 1482-2: Fertilisers and liming materials — Sampling and sample preparation — Part 2: Sample preparation

Methods 2

Nitrogen

Method 2.1

Determination of ammoniacal nitrogen

EN 15475: Fertilisers — Determination of ammoniacal nitrogen
This method of analysis has been ring-tested.

Methods 2.2

Determination of nitric and ammoniacal nitrogen

Method 2.2.1

Determination of nitric and ammoniacal nitrogen according to Ulsch

EN 15558: Fertilisers — Determination of nitric and ammoniacal nitrogen according to Ulsch
This method of analysis has not been ring-tested.

Method 2.2.2

Determination of nitric and ammoniacal nitrogen according to Arnd

EN 15559: Fertilisers – Determination of nitric and ammoniacal nitrogen according to Arnd
This method of analysis has not been ring-tested.

Method 2.2.3

Determination of nitric and ammoniacal nitrogen according to Devarda

EN 15476: Fertilisers — Determination of nitric and ammoniacal nitrogen according to Devarda
This method of analysis has been ring-tested.

Method 2.3

Determination of total nitrogen

Method 2.3.1

Determination of the total nitrogen in calcium cyanamide nitrate free

EN 15560: Fertilisers — Determination of total nitrogen in calcium cyanamide nitrate free
This method of analysis has not been ring-tested.

<div align="center">

Method 2.3.2

Determination of total nitrogen in calcium cyanamide containing nitrates
</div>

EN 15561: Fertilisers — Determination of total nitrogen in calcium cyanamide containing nitrates
This method of analysis has not been ring-tested.

<div align="center">

Method 2.3.3

Determination of total nitrogen in urea
</div>

EN 15478: Fertilisers — Determination of total nitrogen in urea
This method of analysis has been ring-tested.

<div align="center">

Method 2.4

Determination of cyanamide nitrogen
</div>

EN 15562: Fertilisers — Determination of cyanamide nitrogen
This method of analysis has not been ring-tested.

<div align="center">

Method 2.5

Spectrophotometric determination of biuret in urea
</div>

EN 15479: Fertilisers — Spectrophotometric determination of biuret in urea
This method of analysis has been ring-tested.

<div align="center">

Methods 2.6

Determination of different forms of nitrogen in the same sample

Method 2.6.1

**Determination of different forms of nitrogen in the same sample in fertilisers
containing nitrogen as nitric, ammoniacal, urea and cyanamide nitrogen**
</div>

*EN 15604: Fertilisers — Determination of different forms of nitrogen in the same sample containing
nitrogen, as nitric, ammoniacal, urea and cyanamide nitrogen*
This method of analysis has not been ring-tested.

<div align="center">

Method 2.6.2

**Determination of different forms of nitrogen in fertilisers containing
nitrogen only as nitric, ammoniacal and urea nitrogen**
</div>

*EN 15750: Fertilizers. Determination of total nitrogen in fertilizers containing nitrogen only as nitric,
ammoniacal and urea nitrogen by two different methods.*
This method of analysis has been ring-tested.

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Method 2.6.3

**Determination of urea condensates using HPLC — Isobutylenediurea and crotonylidenediurea
(method A) and methylen-urea oligomers (method B)**
</div>

*EN 15705: Fertilizers. Determination of urea condensates using high- performance liquid
chromatography (HPLC). Isobutylenediurea and crotonylidenediurea (method A) and methylen-urea
oligomers (method B)*
This method of analysis has been ring-tested.

<div align="center">

Methods 3
Phosphorus

Methods 3.1
</div>

Extractions

Method 3.1.1
Extraction of phosphorus soluble in mineral acids
EN 15956: Fertilizers – Extraction of phosphorus soluble in mineral acids
This method of analysis has been ring-tested.

Method 3.1.2
Extraction of the phosphorus soluble in 2 % formic acid
EN 15919: Fertilizers – Extraction of phosphorus soluble in 2 % formic acid
This method of analysis has not been ring-tested.

Method 3.1.3
Extraction of phosphorus soluble in 2 % citric acid
EN 15920: Fertilizers – Extraction of phosphorus soluble in 2 % citric acid
This method of analysis has not been ring-tested.

Method 3.1.4
Extraction of phosphorus which is soluble in neutral ammonium citrate
EN 15957: Fertilizers – Extraction of phosphorus which is soluble in neutral ammonium citrate
This method of analysis has been ring-tested.

Method s 3.1.5
Extraction by alkaline ammonium citrate

Me thod 3.1.5.1
Extraction of soluble phosphorus according to Petermann at 65 °C
EN 15921: Fertilizers – Extraction of phosphorus according to Petermann at 65 °C
This method of analysis has not been ring-tested.

Me thod 3.1.5.2
Extraction of the soluble phosphorus according to Petermann at ambient temperature
EN 15922: Fertilizers – Extraction of phosphorus according to Petermann at ambient temperature
This method of analysis has not been ring-tested.

Me thod 3.1.5.3
Extraction of the phosphorus soluble in Joulie's alkaline ammonium citrate
EN 15923: Fertilizers – Extraction of phosphorus in Joulie's alkaline ammonium citrate
This method of analysis has not been ring-tested.

Method 3.1.6
Extraction of water soluble phosphorus
EN 15958: Fertilizers – Extraction of water soluble phosphorus
This method of analysis has been ring-tested.

Method 3.2
Determination of extracted phosphorus
EN 15959: Fertilizers – Determination of extracted phosphorus
This method of analysis has been ring-tested.

Method 4

Potassium

Method 4.1

Determination of the water-soluble potassium content

EN 15477: Fertilisers — Determination of the water-soluble potassium content
This method of analysis has been ring-tested.

Method 5
Carbon dioxide

Method 5.1

Determination of carbon dioxide — Part I: method for solid fertilisers

EN 14397-1: Fertilizers and liming materials. Determination of carbon dioxide. Part I: method for solid fertilisers
This method of analysis has been ring-tested.

Method 6
Chlorine

Method 6.1
Determination of chlorides in the absence of organic material

1- **Scope**

This document defines the procedure for the determination of chloride, in the absence of organic material.

2- **Field of application**

All fertilisers which are free from organic material.

3- **Principle**

The chlorides, dissolved in water, are precipitated in an acid medium by an excess of standard solution of silver nitrate. The excess is titrated with a solution of ammonium thiocyanate in the presence of ferric ammonium sulphate (Volhard's method).

4- **Reagents**

Distilled or demineralised water, free from chlorides.

4-1 Nitrobenzene or diethyl ether

4-2 Nitric acid: 10 mol/l

4-3 Indicator solution

Dissolve 40 g of ferric ammonium sulphate $Fe_2(SO_4)_3$. $(NH_4)_2SO_4$. $24H_2O$, in water and make up to one litre.

4-4 Silver nitrate standard solution: 0,1 mol/l

Preparation

Since this salt is hygroscopic and cannot be dried without risk of decomposition, it is advisable to weigh out approximately 9 g, dissolve in water and make up the volume to one litre. Adjust to 0,1 mol/l strength by titration of AgNO3 0,1 mol/l.

5- **Apparatus**

5-1 Rotary shaker (35 to 40 turns per minute)

5-2 Burettes

5-3 A 500-ml graduated flask

5-4 Conical (Erlenmeyer) flask of 250 ml

6- **Preparation of the sample**

See Method 1.

7- **Procedure**

7-1 Sample and preparation of the solution

Place 5 g of the sample, weighed out to nearest 0,001 g, in a 500-ml graduated flask and add 450 ml of water. Mix for half an hour on the shaker (5-1); make up to 500 ml with distilled water; mix and filter into a beaker.

7-2   Determination

Take an aliquot part of the filtrate containing not more than 0,150 g of chloride. For example 25 ml (0,25 g), 50 ml (0,5 g) or 100 ml (1 g). If the sample taken is smaller than 50 ml it is necessary to make up the volume to 50 ml with distilled water.

Add 5 ml of nitric acid 10 mol/l (4-2), 20 ml of indicator solution (4-3), and two drops of ammonium thiocyanate standard solution (a sample of this latter reagent is taken with a burette adjusted to zero for this purpose).

With a burette then add silver nitrate standard solution (4-4) until there is an excess of 2 to 5 ml. Add 5 ml of nitrobenzene or 5 ml of diethyl ether (4-1) and shake well to agglomerate the precipitate. Titrate the excess silver nitrate with ammonium thiocyanate 0,1 mol/l (4-5) until a red-brown colour appears which remains after the flask has been shaken slightly.

N o t e

Nitrobenzene or diethyl ether (but above all nitrobenzene) prevents the silver chloride from reacting with thiocyanate ions. Thus a clear colour change is obtained.

7-3   Blank test

Carry out a blank test (omitting the sample) under the same conditions and allow for it when calculating the final result.

7-4   Control test

Before carrying out the estimations check the accuracy of the Method by using an aliquot part of a freshly prepared solution of potassium chloride, such that this part contains a known quantity in the order of 100 mg of chloride.

8-   Expression of the result

Express the result of the analysis as a percentage of chloride contained in the sample as it has been received for analysis.

Calculate the percentage of chloride (Cl) with the formula:

$$\% \text{ chloride} = \frac{(Vz - Vcz) - (Va - Vca) \times 100}{M}$$

where

V_z = number of millilitres of silver nitrate 0,1 mol/l,

V_{cz} = number of millilitres of silver nitrate 0,1 mol/l, used in the blank test,

V_a = number of millilitres of ammonium thiocyanate 0,1 mol/l,

V_{ca} = number of millilitres of ammonium thiocyanate 0,1 mol/l, used in the blank test,

M = mass, in grams, of the sample taken (7-2).

<div align="center">

Methods 7

Fineness of grinding

Method 7.1

Determination of fineness of grinding
(dry procedure)

</div>

EN 15928: Fertilizers – Determination of the fineness of grinding (dry procedure)
This method of analysis has not been ring-tested.

<div align="center">

Method 7.2

Determination of the fineness of grinding of soft natural phosphates

</div>

EN 15924: Fertilizers – Determination of the fineness of grinding of soft natural phosphates
This method of analysis has not been ring-tested.

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Methods 8

</div>

Secondary nutrients

Method 8.1

Extraction of total calcium, total magnesium, total sodium and total sulphur
in the form of sulphates

EN 15960: Fertilizers – Extraction of total calcium, total magnesium, total sodium and total sulphur in the forms of sulphates

This method of analysis has not been ring-tested.

Method 8.2

Extraction of total sulphur present in various forms

EN 15925: Fertilizers – Extraction of total sulphur present in various forms

This method of analysis has not been ring-tested.

Method 8.3

Extraction of water-soluble calcium, magnesium, sodium and sulphur
(in the form of sulphates)

EN 15961: Fertilizers – Extraction of water soluble calcium, magnesium, sodium and sulphur (in the form of sulphates)

This method of analysis has not been ring-tested.

Method 8.4

Extraction of water-soluble sulphur where the sulphur is in various forms

EN 15926: Fertilizers – Extraction of water soluble sulphur where the sulphur is in various forms

This method of analysis has not been ring-tested.

Method 8.5

Extraction and determination of elemental sulphur

EN 16032: Fertilizers – Extraction and determination of elemental sulphur

This method of analysis has not been ring-tested.

Method 8.6

Manganimetric determination of extracted calcium following precipitation in
the form of oxalate

1-   Scope

This document defines the procedure for determining the calcium in fertiliser extracts.

2-   Field of application

This Method applies to EC fertilisers for which a declaration of the total and/or water-soluble calcium is provided for in Annex I.

3-   Principle

Precipitation of the calcium contained in an aliquot of the extraction solution in the form of an oxalate, after separation and dissolution of the latter, by titration of oxalic acid using potassium permanganate.

4-   Reagents

4-1   Diluted hydrochloric acid

One volume of hydrochloric acid ($d_{20} = 1,18$ g/ml) and one volume of water.

4-2   1:10 dilute sulphuric acid

One volume of sulphuric acid ($d_{20} = 1,84$ g/ml) in ten volumes of water.

4-3   1:1 dilute ammonia solution

One volume of ammonia ($d_{20} = 0,88$ g/ml) and one volume of water.

4-4   Saturated solution of ammonia oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$] at ambient temperature (approximately 40 grams per litre)

4-5   Citric acid solution, 30 % (m/v)

4-6   Ammonium chloride solution, 5 % (m/v)

4-7   Solution of bromothymol blue in ethanol, at 95 %, 0,1 % (m/v)

4-8   Solution of bromocresol green in ethanol, at 95 %, 0,04 % (m/v)

4-9   Standard solution of potassium permanganate, 0,02 mol/l

5- Apparatus

5-1   Filter crucible with 5 to 20 μ porosity sintered glass

5-2   Hot water bath

6- Preparation of the aliquot to be analysed

Using a pipette, take an aliquot portion of the extraction solution obtained by Method 8.1 or 8.3, containing between 15 and 50 milligrams of Ca (= 21 to 70 milligrams of CaO). Let the volume of this aliquot be v_2. Pour into a 400 millilitre beaker. If necessary, neutralise (turning of indicator (4-7) from green to blue) with a few drops of the ammonia solution (4-3).

Add one millilitre of the citric acid solution (4-5) and five millilitres of ammonium chloride solution (4-6).

7- Precipitation of the calcium oxalate

Add approximately 100 millilitres of water. Bring to the boil, add eight to ten drops of indicator solution (4-8) and, slowly, 50 millilitres of a hot ammonium oxalate solution (4-4). If a precipitate forms, dissolve by adding a few drops of hydrochloric acid (4-1). Neutralise very slowly with ammonia solution (4-3) while stirring continuously to a pH of 4,4 to 4,6 (turning of indicator (4-8) from green to blue). Place the beaker in a boiling hot water bath (5-2) for approximately 30 minutes.

Remove the beaker from the bath, leave standing for an hour and filter into the crucible (5-1).

8- Titration of the oxalate precipitate

Wash the beaker and crucible until the excess ammonium oxalate has been completely removed (this can be checked by the absence of chloride in the washing water). Place the crucible in the 400 millilitre beaker and dissolve the precipitate with 50 millilitres of hot sulphuric acid (4-2). Add water to the beaker in order to obtain a volume of approximately 100 millilitres. Bring to a temperature of 70 to 80 °C and titrate drop by drop with a permanganate solution (4-9) until the pink colour lasts for a minute. Let this volume be n.

9- Expression of results

The calcium (Ca) content of the fertiliser is as follows:

$$Ca\ (\%) = n \times 0.2004 \times \frac{t}{0.02} \times \frac{v1}{v2 \times m}$$

Where

n = the number of millilitres of permanganate used,

m = the mass of the test sample in grams,

v_2 = the aliquot volume in millilitres,

v_1 = the volume of the extraction solution in millilitres,

t = the concentration of the permanganate solution in moles per litre.

CaO (%) = Ca (%) × 1,400

Method 8.7

Determination of magnesium by atomic absorption spectrometry

1- Scope

This document defines the procedure for determining the magnesium in fertiliser extracts.

2- Field of application

This Method applies to EC fertiliser extracts obtained by methods 8.1 and 8.3, for which a declaration of the total magnesium and/or water soluble magnesium is required, with the exception of the following fertilisers listed in Annex I D relating to secondary nutrients:

−   type 4 (kieserite),

−   type 5 (magnesium sulphate) and type 5-1 (magnesium sulphate solution),

- and with the exception of the following fertiliser listed in Annex I A 3 relating to potassic fertilisers:
- type 7 (kieserite with potassium sulphate)
- to which Method 8.8 applies.

The Method set out below applies to all fertiliser extracts containing elements in quantities that might interfere with the complexometric determination of magnesium.

3- Principle

Determination of magnesium by atomic absorption spectrometry after appropriate dilution of the extract.

4- Reagents

4-1 Hydrochloric acid, 1 mol/l solution

4-2 Hydrochloric acid, 0,5 mol/l solution

4-3 Standard solution of magnesium, 1,00 milligrams per millilitre

4-3-1 Dissolve 1,013 grams of magnesium sulphate ($MgSO_4$, $7H_2O$) in the 0,5 mol/l hydrochloric acid solution (4-2)

4-3-2 Weigh out 1,658 grams of magnesium oxide (MgO), previously calcined to remove all traces of carbonation. Place in a beaker with 100 millilitres of water and 120 millilitres of 1 mol/l hydrochloric acid (4-1). When it has dissolved, decant quantitatively into a 1 000 millilitre graduated flask. Make up the volume by adding and mix

or

4-3-3 Commercial standard solution

The laboratory is responsible for testing such solutions.

4-4 Strontium chloride solution

Dissolve 75 grams of strontium chloride ($SrCl_2$ $6H_2O$) in a hydrochloric acid solution (4.2) and make up to 500 millilitres with the same acid solution.

5- Apparatus

Spectrometer fitted for atomic absorption, with a magnesium lamp, set at 285,2 nm. Air-acetylene flame.

6- Preparation of the sample

See Methods 8.1 and 8.3.

7- Procedure

7-1 If the fertiliser has a declared magnesium (Mg) content of more than 6 % (i.e. 10 % as MgO), take 25 millilitres (V_1) of the extraction solution (6). Transfer into a 100 millilitre graduated flask, and make up to volume with water and mix. The dilution factor is $D_1 = 100/V_1$

7-2 Using a pipette, take 10 millilitres of the extraction solution (6) or the solution (7-1). Transfer into a 200 millilitre graduated flask. Make up to volume with the 0,5 mol/l hydrochloric acid solution (4-2) and mix.

The dilution factor is 200/10

7-3 Dilute this solution (7-2) with the 0,5 mol/l hydrochloric acid solution (4-2) so as to obtain a concentration in the optimum working field of the spectrometer (5-1). V_2 is the volume of the sample in 100 millilitres. The dilution factor is $D_2 = 100/V_2$

The final solution should contain 10 % v/v of the strontium chloride solution (4-4).

7-4 Preparation of blank solution

Prepare a blank solution by repeating the whole procedure from the extraction (Method 8.1 or 8.3), omitting only the test sample of fertiliser.

7-5 Preparation of calibration solutions

By diluting the standard solution (4-3) with the 0,5 mol/l hydrochloric acid, prepared at least five calibration solutions of increasing concentration within the optimum measuring range of the apparatus (5-1).

These solutions should contain 10 % v/v of the strontium chloride solution (4-4).

7-6   Measurement

Set up the spectrometer (5-1) at a wavelength of 285,2 nm. Spray, successively, the calibration solutions (7-5), the sample solution (7-3) and the blank solution (7-4), washing the instrument through with the solution to be measured next. Repeat this operation three times. Plot the calibration curve using the mean absorbancies of each of the calibrations (7-5) as the ordinates and the corresponding concentration of magnesium in µg/ml as the abscissae. Determine the concentration of magnesium in the sample (7-3), Xs and blank (7-4), Xb, by reference to the calibration curve.

8-   Expression of results

Calculate the amount of magnesium (Mg) or magnesium oxide (MgO) in the sample by reference to the calibration solutions and taking into consideration the blank.

The percentage of magnesium (Mg) in the fertiliser is equal to:

$$Mg\ (\%) = \frac{(Xs - Xb)D1\left(\frac{200}{10}\right)D2\ 500.100}{1000.1000M}$$

Where

X_s = the concentration of the solution to be analysed recorded on the calibration curve, in µg/ml.

X_b = the concentration of the blank solution as recorded on the calibration curve, in µg/ml.

D_1 = the dilution factor when the solution is diluted (7-1).

−   It is equal to four if 25 millilitres are taken.

−   It is equal to one when the solution is not diluted.

− D_2 = the dilution factor is 7-3.

−   M = the mass of the test sample at the time of extraction.

−   MgO (%) = Mg (%)/0,6

Method 8.8

Determination of magnesium by complexometry

1-   Scope

This document defines the procedure for the determination of magnesium in fertiliser extracts.

2-   Field of application

This Method applies to the following EC fertiliser extracts for which the determination of total magnesium and/or water-soluble magnesium is provided for:

−   fertilisers listed in Annex I: straight nitrogenous fertilisers, type 1b + 1c (calcium magnesium nitrate), type 7 (magnesium sulphonitrate), type 8 (nitrogenous fertilisers with magnesium) and straight potassic fertilisers, type 2 (enriched kainite), type 4 (potassium chloride containing magnesium), type 6 (potassium sulphate containing magnesium salt),

−   fertilisers listed in the Annex I D relating to secondary nutrients.

3-   Principle

The magnesium is solubilised by methods 8.1 and/or 8.3. First titration: with EDTA of Ca and Mg in the presence of Eriochrome black-T. Second titration: with EDTA of Ca in the presence of calcein or of calcon carbonic acid. Determination of magnesium by difference.

4-   Reagents

4-1   Standard 0,05 mol/l solution of magnesium:

4-1-1   Dissolve 1,232 grams of magnesium sulphate ($MgSO_4$ $7H_2O$) in the 0,5 mol/l hydrochloric acid solution (4-11) and make up to 100 millilitres with the same acid

or

4-1-2   Weigh out 2,016 grams of magnesium oxide, previously calcined to remove all traces of carbonation. Place it in a beaker with 100 millilitres of water

Stir in approximately 120 millilitres of approximately 1 mol/l hydrochloric acid (4-12).

After dissolution, transfer quantitatively into a graduated 1 000 millilitre flask. Make up to volume and mix.

One millilitre of these solutions should contain 1,216 milligrams of Mg (= 2,016 milligrams of MgO).

The laboratory is responsible for testing the strength of this standard solution.

4-2   0,05 molar solution of EDTA

Weigh out 18,61 grams of the dihydrated disodium salt of ethylenediaminetetraacetic ($C_{10}H_{14}N_2Na_2O_8.2H_2O$), place it in a 1 000 millilitre beaker and dissolve in 600 to 800 millilitres of water. Transfer the solution quantitatively into a graduated 1 000 millilitre flask. Make up the volume and mix. Check this solution with the standard solution (4-1) by taking a sample of 20 millilitres of the latter and by titration according to the analytical procedure described at (7-2).

One millilitre of the EDTA solution should correspond to 1,216 milligrams of Mg (= 2,016 milligrams of MgO) and to 2,004 milligrams of Ca (= 2,804 milligrams CaO) (see remarks 10,1 and 10,6).

4-3   0,05 molar standard solution of calcium

Weigh out 5,004 grams of dry calcium carbonate. Place it in a beaker with 100 millilitres of water. Progressively stir in 120 millilitres of approximately 1 mol/l hydrochloric acid (4-12).

Bring to the boil in order to drive off the carbon dioxide, cool, transfer quantitatively into a graduated one-litre flask, make up the volume with water and mix. Check this solution against the EDTA solution (4-2) following analytical procedure (7-3). One millilitre of this solution should contain 2,004 milligrams of Ca (= 2,804 milligrams of CaO) and should correspond to one millilitre of the 0,05 molar EDTA solution (4-2).

4-4   Calcein indicator

Carefully mix in a mortar one gram of calcein with 100 grams of sodium chloride. Use 10 milligrams of this mixture. The indicator changes from green to orange. Titration must be carried out until an orange is obtained which is free from green tinges.

4-5   Calcon carbonic acid indicator

Dissolve 400 milligrams of calcon carbonic acid in 100 millilitres of methanol. This solution may only be kept for approximately four weeks. Use three drops of this solution. The indicator changes from red to blue. Titration must be carried out until a blue is obtained which is free from red tinges.

4-6   Eriochrome black-T indicator

Dissolve 300 milligrams of Eriochrome black-T in a mixture of 25 millilitres of propanol-1 and 15 millilitres of triethanolamine. This solution may only be kept for approximately four weeks. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue is obtained which is free from red tinges. It changes colour only when magnesium is present. If necessary add one millilitre of the standard solution (4-1).

When both calcium and magnesium are present the EDTA first forms a complex with the calcium and then with the magnesium. In that case two elements are determined concurrently.

4-7   Potassium cyanide solution

Aqueous solution of KCN at 2 %. (Do not pipette by mouth and see 10.7).

4-8   Solution of potassium hydroxide and potassium cyanide

Dissolve 280 grams of KOH and 66 grams of KCN in water, make up the volume to one litre and mix.

4-9   pH 10,5 buffer solution

In a 500 millilitre graduated flask, dissolve 33 grams of ammonium chloride in 200 millilitres of water, add 250 millilitres of ammonia (d_{20} = 0,91 g/ml) make up the volume with water and mix. Test the pH of
the solution regularly.

4-10   Diluted hydrochloric acid: one volume of hydrochloric acid (d_{20} = 1,18 g/ml) plus one volume of water

4-1-1   Hydrochloric acid solution approximately 0,5 mol/l

4-1-2   Hydrochloric acid solution approximately 1 mol/l

4-1-3   Sodium hydroxide solution 5 mol/l

5-   Apparatus

5-1   Magnetic or mechanical stirrer

5-2   pH meter

6-   Control test

Carry out a determination on aliquot parts of solutions (4-1 and 4-3) such that the Ca/Mg ratio is approximately equal to that of the solution to be analysed. To this end take (a) millilitres of Mg standard solution (4-3) and (b-a) millilitres of standard solution (4-1) (a) and (b) are the numbers of millilitre EDTA solution used in the two titrations performed on the solution to be analysed. This procedure is correct only if the solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make corrections.

7-   Preparation of the solution to be analysed

See methods 8.1 and 8.3.

8-   Determination

8-1   Aliquot samples to be taken

The aliquot part will as far as possible contain between 9 and 18 milligrams of magnesium (= 15 to 30 milligrams of MgO).

8-2   Titration in the presence of Eriochrome black-T

Pipette an aliquot part (8-1) of the solution to be analysed into a 400 millilitre beaker. Neutralise the surplus acid with the 5 mol/l sodium hydroxide solution (4-12) using the pH meter. Dilute with water to approximately 100 millilitres. Add 5 millilitres of the buffer solution (4-9). The pH measured by the meter must be 10,5 ± 0,1. Add 2 millilitres of the potassium cyanide solution (4.7) and three drops of the Eriochrome black-T indicator (4-6). Titrate with the EDTA solution (4-2). Stirring gently with the stirrer (5-1) (see 10,2, 10,3 and 10,4). Let 'b' be the number of millilitres of 0,05 mol/l EDTA solution.

8-3   Titration in the presence of calcein or of calcon carbonic acid

Pipette an aliquot part of the solution to be analysed equal to that taken from the above titration and place it in a 400 millilitre beaker. Neutralise the surplus acid with the 5 mol/l sodium hydroxide solution (4-13) using the pH meter. Dilute with water to about 100 millilitres. Add 10 millilitres of the KOH/KCN solution (4-8) and the indicator (4-4 or 4-5). Stirring gently with the stirrer (5-1) titrate with the EDTA solution (4-2) (see 10,2, 10,3 and 10,4). Let 'a' be the number of millilitres of 0,05 mol/l EDTA solution.

9-   Expression of the results

For the EC fertilisers to which the Method is applicable (5 grams of fertiliser in 500 millilitres of extract), the percentage content of the fertiliser is:

$$\text{MgO (\%)in the} = \frac{(b - a) \times T}{M}$$

$$\text{Mg (\%)in the} = \frac{(b - a) \times T'}{M}$$

Where

a = the number of millilitres of 0,05 mol/l EDTA solution used for the titration in the presence of calcein or calcon carbonic acid,

b = the number of millilitres of 0,05 mol/l EDTA solution used for the titration in the presence of Eriochrome black-T,

M = the mass of the sample present in the aliquot part taken (in grams),

T = 0,2016 × mol/l of the EDTA solution/0,05 (see 4.2),

T′ = 0,1216 × mol/l of the EDTA solution/0,05 (see 4.2).

10- Remarks

10-1 The stoichiometric EDTA-metal ratio in the complexometric analyses is always 1:1 whatever the valency of the metal and in spite of the fact that EDTA is quadrivalent. The EDTA titration solution and the standard solutions will therefore be molar and not normal

10-2 Complexometric indicators are often sensitive to air. The solution may lose colour during titration. In this case, one or two drops of indicator must be added. This is true particularly in the case of eriochrome black and calcon carbonic acid

10-3 The metal-indicator complexes are often relatively stable and it may take some time for the colour to change. The last drops of EDTA must therefore be added slowly and a drop of 0,05 mol/l solution of magnesium (4-1) or calcium (4-3) added to ensure that the colour change has not already taken place. This is particularly true in the case of the eriochrome-magnesium complex

10-4 The turning of the indicator must be observed not vertically, but horizontally across the solution and the beaker must be placed against a white background in a well-lit position. The turning of the indicator may also be observed easily by placing the beaker on frosted glass lit moderately from below (25 watt lamp)

10-5 This analysis requires a certain amount of experience. The task will involve, inter alia, observing the colour changes of standard solutions 4-1 and 4-3. It is recommended that the determinations be carried out by the same laboratory chemist

10-6 If an EDTA solution of guaranteed strength is used (Titrisol, Normex, for example) this may simplify the control of the equivalence of standard solutions 4-1, 4-2 and 4-3

10-7 The solutions containing potassium cyanide must not be poured down the sink until the cyanide has been converted into a harmless compound, for example, by oxidization with sodium hypochlorite following alkalization

Method 8.9
Determination of the sulfates content using three different methods
EN 15749: Fertilizers. Determination of sulfates content using three different methods
This method of analysis has been ring-tested.

Method 8.10
Determination of the sodium extracted

1- Scope
This document defines the procedure for determining the sodium in fertiliser extracts.

2- Field of application
This Method applies to EC fertilisers for which a declaration of the sodium is provided for in Annex I.

3- Principle
Following suitable dilution of the extract obtained via Method 8.1 and/or 8.3, the sodium content of the solution is determined by flame-emission spectrometry.

4- Reagents

4-1 Diluted hydrochloric acid
One volume of hydrochloric acid for analysis (d_{20} = 1,18 g/ml) plus one volume of water.

4-2 Aluminium nitrate $Al(NO_3)_3.9H_2O$

4-3 Caesium chloride, $CsCl$

4-4 Anhydrous sodium chloride, $NaCl$

4-5 Caesium chloride and aluminium nitrate solution
Dissolve in water 50 grams of caesium chloride (4-3) and 250 grams of aluminium nitrate (4-2) in a 1 000 millilitre graduated flask. Make up to volume with water and mix.

4-6 Standard sodium solution of one milligram/millilitre of Na
Dissolve in water 2,542 grams of sodium chloride (4-4) in a 1 000 millilitre graduated flask. Add 10 millilitres of hydrochloric acid (4-1). Make up to volume with water and mix.

5- Apparatus

Spectrometer equipped for flame emission, set at 589,3 nm.

6- Calibration solutions

6-1 Place 10 millilitres of standard solution (4-6) in a 250 millilitre graduated flask. Make up to volume and mix. Concentration of solution: 40 µg/ml of Na

6-2 Place 0, 5, 10, 15, 20, 25 millilitres of the intermediate solution (6-1) in 100 millilitre graduated flasks. Add 10 millilitres of the solution (4-5). Make up to volume and mix. Concentration of solutions: 0, 2, 4, 6, 8, 10 µg/ml of Na

7- Preparation of solutions to be measured

Depending upon the expected sodium content of the extraction solution as in Method 8.1 or 8.3 (five grams of fertiliser in 500 millilitres), carry out the dilutions in accordance with the following table:

Na_2O (%)	Na (%)	Intermediate dilution		Final dilution		Degree of dilution
		Sample (ml) (v_2)	Dilution to ml (v_3)	Sample (ml) (v_4)	Dilution to ml	
3-5	2,2-3,7	10	50	10	100	50
5-10	3,7-7,4	10	100	10	100	100
10-20	7,4-15	10	100	5	100	200
20-38	15-28	5	100	5	100	400

Make up the intermediate dilution with water. For the final dilution add ten millilitres of the solution (4-5) to the 100 millilitre graduated flask.

For a test sample of one gram multiply the volume of the final dilution (v_4) by five.

8- Determination

Prepare the spectrometer (5-1) for the measurements at 589,3 nm. Calibrate the instrument by measuring the response of the calibration solutions (6-2). Then adjust the sensitivity of the instrument to use its entire scale when the most concentrated calibration solution is used.

Then measure the response of the sample solution to be analysed (7). Repeat this operation three times.

9- Calculation of results

Draw a calibration curve by plotting the average response for each calibration solution along the ordinate and the corresponding concentrations, expressed in µg per millilitre on the abscissa. Determine from this the sodium concentration of the test solution. Calculate the

quantity of sodium from the standard solutions taking account of the levels of dilution. Express the results as a percentage of the sample.

The percentage sodium (Na) content of the fertiliser is as follows:

$$Na\ \% = x.\frac{v3}{v4}\frac{v1}{v2}\frac{10^{-2}}{m}$$
$$Na2O\ \% = Na\ \% \times 1.348$$

Where

x = the concentration of the solution introduced into the spectrometer in μg/ml,

v_1 = the volume of the extraction solution in millilitres,

v_2 = the aliquot volume in the intermediate dilution in millilitres,

v_3 = the volume of intermediate dilution in millilitres,

v_4 = the aliquot volume in ml of the final dilution (to 100 millilitres),

m = the mass of the test sample in grams.

Method 8.11
Determination of calcium and formate in calcium formate
EN 15909: Fertilizers – Determination of calcium and formate in calcium foliar fertilizers

This method of analysis has been ring-tested.

Methods 9
Micro-nutrients at a concentration of less than or equal to 10 %

Method 9.1
Extraction of total micro-nutrients

1- Scope

This Method defines the procedure for extracting the following micro-nutrients: total boron, total cobalt, total copper, total iron, total manganese, total molybdenum and total zinc. The aim is to carry out the minimum number of extractions, making use wherever possible of the same extract to determine the total level of each of the micro-nutrients listed above.

2- Field of application

This procedure concerns EC fertilisers covered by Annex I E containing one or more of the following micro-nutrients: boron, cobalt, copper, iron, manganese, molybdenum and zinc. It is applicablemto each micro-nutrient the declared content of which is less than or equal to 10 %.

3- Principle

Dissolution in boiling dilute hydrochloric acid.

N o t e

The extraction is empirical and may not be quantitative depending on the product or the other constituents of the fertiliser. In particular, in the case of certain manganese oxides, the quantity extracted may be substantially smaller than the total quantity of manganese which the product contains. It is the responsibility of the fertiliser manufacturers to ensure that the declared content actually corresponds to the quantity extracted under the conditions pertaining to the method.

4- Reagents

4-1   Dilute hydrochloric acid (HCl) solution, about 6 mol/l

Mix 1 volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 1 volume of water.

4-2   Concentrated ammonia solution (NH_4OH, d_{20} = 0,9 g/ml)

5- Apparatus

Electric hotplate with variable temperature control.

N o t e

Where the boron content of an extract is to be determined, do not use borosilicate glassware. As the Method involves boiling, teflon or silica is preferable. Rinse the glassware thoroughly if it has been washed in detergents containing borates.

6- **Preparation of the sample**

See Method 1.

7- **Procedure**

7-1 Test sample

Take a quantity of fertiliser weighing between 2 and 10 g depending on the declared content of element in the product. The following table shall be used to obtain a final solution which, after appropriate dilution, will be within the measuring range for each method. Samples should be weighed to within 1 mg.

Declared content of micro-nutrient in the fertiliser (%)	< 0,01	0,01< 5	≥ 5-10
Mass of test sample (g)	10	5	2
Mass of element in the sample (mg)	1	0,5-250	100-200
Volume of extract V (ml)	250	500	500
Concentration of element in extract (mg/l)	4	1-500	200-400

Place the sample in a 250 ml beaker.

7-2 Preparation of the solution

If necessary moisten the sample with a little water, add 10 ml of dilute hydrochloric acid (4-1) per gram of fertiliser carefully, in small amounts, then add about 50 ml of water. Cover the beaker with a watch glass and mix. Bring to the boil on the hotplate and boil for 30 minutes. Allow to cool, stirring occasionally. Transfer quantitatively to a 250 or 500 ml volumetric flask (see Table). Make up to volume with water and mix thoroughly. Filter through a dry filter into a dry container. Discard the first portion. The extract must be perfectly clear.

It is recommended that the determination be carried out without delay on aliquot portions of the clear filtrate, if not the containers should be stoppered.

R e m a r k

Extracts in which the boron content has to be determined: Adjust the pH to between 4 and 6 with concentrated ammonia (4-2).

8- **Determination**

The determination of each micro-nutrient is to be carried out on the aliquot portions indicated in the Method for each individual micro-nutrient.

If necessary, remove organic chelating or complexing substances from an aliquot portion of the extract by using Method 9.3. In the case of determination by atomic absorption spectrometry, such removal may not be necessary.

Method 9.2

Extraction of water-soluble micro-nutrients

1- **Scope**

This Method defines the procedure for extracting water-soluble forms of the following micro-nutrients: boron, cobalt, copper, iron, manganese, molybdenum and zinc. The aim is to carry out the minimum number of extractions, making use wherever possible of the same extract to determine the level of each of the micro-nutrients listed above.

2- **Field of application**

This procedure concerns EC fertilisers covered by Annex I containing one or more of the following micro-nutrients: boron, cobalt, copper, iron, manganese, molybdenum and zinc. It is applicable to each micro-nutrient the declared content of which is less than or equal to 10 %.

3-   Principle

The micro-nutrients are extracted by shaking the fertiliser in water at 20 °C (± 2) °C.

N o t e

The extraction is empirical and may or may not be quantitative.

4-   Reagents

4-1   Dilute hydrochloric acid (HCl) solution, about 6 mol/l

Mix 1 volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 1 volume of water.

5-   Apparatus

5-1   Rotary shaker set at about 35 to 40 rpm

5-2   pH-meter

N o t e

Where the boron content of the extract is to be determined, do not use borosilicate glassware. Teflon or silica is preferable for this extraction.

Rinse the glassware thoroughly if it has been washed in detergents containing borates.

6-   Preparation of the sample

See Method 1.

7-   Procedure

7-1   Test sample

Take a quantity of fertiliser weighing between 2 and 10 g depending on the declared content of the element in the product. The following table shall be used to obtain a final solution which, after appropriate dilution, will be within the measuring range for each method. The samples should be weighed to within 1 mg.

Declared content of micro-nutrient in the fertiliser (%)	< 0,01	0,01-< 5	≥ 5-10
Mass of test sample (g)	10	5	2
Mass of element in the sample (mg)	1	0,5-250	100-200
Volume of extract V (ml)	250	500	500
Concentration of element in extract (mg/l)	4	1-500	200-400

Place the sample in a 250 or 500 ml flask (according to the Table).

7-2   Preparation of the solution

Add about 200 ml of water to the 250 ml flask or 400 ml of water to the 500 ml flask. Stopper the flask well. Shake vigorously by hand to disperse the sample, then place the flask on the shaker and shake for 30 minutes. Make up to volume with water and mix thoroughly.

7-3   Preparation of the test solution

Filter immediately into a clean, dry flask. Stopper the flask. Carry out the determination immediately after filtering.

N o t e

If the filtrate gradually becomes cloudy, make another extraction following 7-1 and 7-2 in a flask of volume V_e. Filter into a calibrated flask of volume W which has previously been dried and has received 5,00 ml of dilute hydrochloric acid (4-1).

Stop the filtration at the exact moment when the calibration mark is reached. Mix thoroughly.

Under these conditions the value of V in the expression of results is:

$$V = Ve \times W/(W - 5)$$

The dilutions in the expression of results depend on this value of V.

8-   Determination

The determination of each micro-nutrient is carried out on the aliquot portions indicated in the Method for each individual micro-nutrient.

If necessary, remove organic chelating or complexing substances from an aliquot portion by using Method 9.3. In the case of determination by atomic absorption spectrometry, such removal may not be necessary.

Method 9.3
Removal of organic compounds from fertiliser extracts

1-   Scope

This Method defines a procedure for removing organic compounds from fertiliser extracts.

2-   Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble element is required by Annex I E to this Regulation.

N o t e

The presence of small quantities of organic matter usually does not affect determination by means of atomic absorption spectrometry.

3-   Principle

The organic compounds in an aliquot portion of the extract are oxidised with hydrogen peroxide.

4-   Reagents

4-1   Dilute hydrochloric acid (HCl) solution, about 0,5 mol/l

Mix 1 volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 20 volumes of water.

4-2   Hydrogen peroxide solution (30 % H_2O_2, d_{20} = 1,11 g/ml), free from micro-nutrients

5-   Apparatus

Electric hotplate with variable temperature control.

6-   Procedure

Take 25 ml of the extract solution obtained by Method 9.1 or Method 9.2 and place in a 100 ml beaker. In the case of Method 9.2, add 5 ml of the dilute hydrochloric acid solution (4-1). Then add 5 ml of the hydrogen peroxide solution (4-2). Cover with a watch glass. Allow oxidation to occur at room temperature for about one hour, then bring

gradually to boiling and boil for half an hour. If necessary, add a further 5 ml of the hydrogen peroxide to the solution once it has cooled. Then boil to remove the excess hydrogen peroxide. Allow to cool and transfer quantitatively to a 50 ml volumetric flask and make up to volume. Filter where necessary.

Account should be taken of this dilution when taking aliquot portions and calculating the percentage of micro-nutrient in the product.

Method 9.4
Determination of micro-nutrients in fertiliser extracts by atomic absorption spectrometry
(general procedure)

1-   Scope

This document defines a general procedure for determining the levels of certain micro-nutrients in fertiliser extracts by atomic absorption spectrometry.

2-   Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble element is required by Annex I E to this Regulation.

Adaptations of this procedure for the various micro-nutrients are detailed in the methods defined specifically for each element.

N o t e

In most cases the presence of small quantities of organic matter will not affect determinations by atomic absorption spectrometry.

3- Principle

After the extract has been treated where necessary to reduce or eliminate interfering chemical species, the extract is diluted so that its concentration is in the optimum range of the spectrometer at a wave-length suitable for the micro-nutrient to be determined.

4- Reagents

4-1   Dilute hydrochloric acid solution (HCl), about 6 mol/l:

Mix one volume of hydrochloric acid (d_{20} = 1,18 g/ml) with one volume of water.

4-2   Dilute hydrochloric acid solution (HCl), about 0,5 mol/l:

Mix one volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 20 volumes of water.

4-3   Lanthanum salt solutions (10 g of La per litre)

This reagent is used for determinations of cobalt, iron, manganese and zinc. It can be prepared either:

(a)   with lanthanum oxide dissolved in hydrochloric acid (4-1). Place 11,73 g of lanthanum oxide (La_2O_3) in 150 ml of water in a one litre volumetric flask and add 120 ml of 6 mol/l hydrochloric acid (4-1). Allow to dissolve and then make up to 1 litre with water and mix thoroughly. This solution is approximately 0,5 mol/l in hydrochloric acid

(b)   or with solutions of lanthanum chloride, sulphate or nitrate.

Dissolve 26,7 g of lanthanum chloride heptahydrate ($LaCl_3.7H_2O$) or 31,2 g of lanthanum nitrate hexahydrate [$La(NO_3)_3.6H_2O$] or 26,2 g of lanthanum sulphate nonahydrate [$La_2(SO_4)_3.9H_2O$] in 150 ml of water, then add 85 ml of 6 mol/l hydrochloric acid (4-1). Allow to dissolve and then make up to 1 litre with water. Mix thoroughly. This solution is approximately 0,5 mol/l in hydrochloric acid.

4-4   Calibration solutions

For the preparation of these, see the individual determination Method for each micro-nutrient.

5- Apparatus

Atomic absorption spectrometer fitted with sources emitting radiation characteristic of the micro-nutrients to be determined.

The analyst must follow the manufacturer's instructions and be familiar with the apparatus. The apparatus must allow background correction so that it can be used whenever necessary (Co and Zn). The gases to be used are air and acetylene.

6- Preparation of the solution to be analysed

6-1   Preparation of extract solutions of the micro-nutrients to be determined.

See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2   Treatment of the test solution

Dilute an aliquot portion of the extract obtained by Method 9.1, 9.2 or 9.3 with water and/or hydrochloric acid (4-1) or (4-2) so as to obtain, in the final solution for measurement, a concentration of the element to be determined that is appropriate to the calibration range used (7-2) and a hydrochloric acid concentration of at least 0,5 mol/l and not more than 2,5 mol/l. This operation may require one or more successive dilutions.

Take an aliquot portion of the final solution obtained by dilution of the extract, let (a) be its volume in ml, and pour into a 100 ml volumetric flask. When determining the cobalt, iron, manganese or zinc content, add 10 ml of the lanthanum salt solution (4.3). Make up to volume with the 0,5 mol/l hydrochloric acid solution (4.2) and mix thoroughly.

This is the final solution for measurement. Let D be the dilution factor.

7- Procedure

7-1 Preparation of a blank solution

Prepare a blank solution by repeating the whole procedure from the extraction stage, omitting only the test sample of fertiliser.

7-2 Preparation of calibration solutions

From the working calibration solution prepared using the Method given for each individual micro-nutrient, prepare in 100 ml volumetric flasks a series of at least five calibration solutions of increasing concentration within the optimum measuring range of the spectrometer. If necessary, adjust the concentration of hydrochloric acid to bring it as close as possible to that of the diluted test solution (6-2).

For determining cobalt, iron, manganese or zinc, add 10 ml of the same lanthanum salt solution (4-3) as used in 6-2. Make up to volume with the 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

7-3 Determination

Prepare the spectrometer (5) for the determination and adjust to the wavelength given in the Method for the individual micro-nutrient concerned.

Spray three times in succession the calibration solutions (7-2), the test solution (6-2) and the blank solution (7-1), noting each result and flushing the instrument with distilled water between individual sprayings.

Construct the calibration curve by plotting the average spectrometer reading for each calibration solution (7-2) along the ordinate and the corresponding concentration of the element, expressed in μg/ml, along the abscissa.

From this curve, determine the concentrations of the relevant micro-nutrient in the test solution x_s (6-2) and in the blank solution x_b(7-1), expressing these concentrations in μg per ml.

8- Expression of results

The percentage of micro-nutrient (E) in the fertiliser is equal to:

$$E(\%) = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$

If Method 9.3 has been used:

$$E(\%) = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$

Where

E is the amount of the micro-nutrient determined, expressed as a percentage of the fertiliser;

x_s is the concentration of the test solution (6-2), in μg/ml;

x_b is the concentration of the blank solution (7-1), in μg/ml;

V is the volume of the extract obtained by Method 9.1 or 9.2, in ml;

D is the factor corresponding to the dilution carried out in 6-2;

M is the mass of the test sample taken in accordance with Method 9.1 or 9.2, in grams.

Calculation of dilution factor D:

If (a1), (a2), (a3),.,.,., (ai) and (a) are the aliquot portions and (v_1), (v_2), (v_3),.,.,., (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D will be equal to:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times.\times.\times.\times (Vi/ai) \times (100/a)$$

Method 9.5

Determination of boron in fertiliser extracts by means of spectrometry with azomethine-H

1- **Scope**

This Method describes a procedure for determining boron in fertilizer extracts.

2- **Field of application**

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble boron is required by Annex I to this Regulation.

3- **Principle**

In an azomethine-H solution, borate ions form a yellow complex the concentration of which is determined by molecular absorption spectrometry at 410 nm. Interfering ions are masked with EDTA.

4- **Reagents**

4-1   EDTA buffer solution

Place in a 500 ml volumetric flask containing 300 ml of water:

− 75 g of ammonium acetate (NH_4OOCCH_3);

− 10 g of disodium salt of ethylene diamine tetraacetic acid (Na_2EDTA);

− 40 ml of acetic acid (CH_3COOH, d_{20} = 1,05 g/ml).

Make up to volume with water and mix thoroughly. The pH of the solution, checked by means of a glass electrode, must be $4,8 \pm 0,1$.

4-2   Azomethine-H solution

Place in a 200 ml volumetric flask

− 10 ml of the buffer solution (4-1);

− 400 mg of azomethine-H ($C17H12NNaO8S2$);

− 2 g of absorbic acid ($C6H8O6$);

− Make up to volume and mix thoroughly. Do not prepare large quantities of this reagent as it is stable for only a few days.

4-3   Boron calibration solutions

4-3-1   Boron stock solution (100 μg/ml)

Dissolve 0,5719 g of boric acid (H_2BO_3) in water in a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly. Transfer to a plastic bottle for storage in a refrigerator.

4-3-2   Boron working solution (10 μg/ml)

Place 50 ml of stock solution (4-3-1) in a 500 ml volumetric flask. Make up to volume with water and mix thoroughly.

5- **Apparatus**

Spectrometer fitted for molecular absorption with cells having a 10 mm optical path and set to a wavelength of 410 nm.

6- **Preparation of the solution to be analysed**

6-1   Preparation of the boron solution

See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2   Preparation of the test solution

Dilute an aliquot portion of extract (6-1) to obtain a boron concentration as specified in 7-2. Two successive dilutions may be necessary. Let D be the dilution factor.

6-3   Preparation of the correction solution

If the test solution (6-2) is coloured, prepare a corresponding correction solution by placing in a plastic flask 5 ml of test solution (6-2), 5 ml of EDTA buffer solution (4-1) and 5 ml of water and mix thoroughly.

7- **Procedure**

7-1   Preparation of the blank solution

Prepare a blank solution by repeating the whole procedure from the extraction stage, omitting only the test sample of fertiliser.

7-2   Preparation of the calibration solutions

Transfer 0, 5, 10, 15, 20 and 25 ml of the working calibration solution (4-3-3) to a series of 100 ml volumetric flasks. Make up to 100 ml with water and mix thoroughly. These solutions contain between 0 and 2,5 μg/ml of boron.

7-3 Colour development

Transfer 5 ml of the calibration solutions (7-2), test solutions (6-2) and blank (7-1) to a series of plastic flasks. Add 5 ml of the EDTA buffer solution (4-1). Add 5 ml of the azomethine-H solution (4-2).

Mix thoroughly and allow the colour to develop in the dark for 21/2 to three hours.

7-4 Determination

Measure the absorbance of the solutions obtained at 7-3 and if appropriate the correction solution (6-3) against water at a wavelength of 410 nm. Rinse the cells with water before each new reading.

8- Expression of results

Plot a calibration curve of the concentration of the calibration solutions (7-2) along the abscissa and the absorbance given by the spectrometer (7-4) along the ordinate.

Read off the calibration curve the concentration of boron in the blank (7-1), the concentration of boron in the test solution (6-2) and, if the test solution is coloured, the corrected concentration of the test solution. To calculate the latter, subtract the absorbance of the correction solution (6-3) from the absorbance of the test solution (6-2) and determine the corrected concentration of the test solution. Note the concentration of the test solution (6-2), with or without correction, $X(x_s)$ and of the blank (x_b).

The percentage of boron in the fertiliser is given by:

$$B\% = ((X_s - X_b) \times V \times D)/(M \times 10^4)$$

If Method 9.3 is used:

$$B\% = ((X_s - X_b) \times V \times 2D)/(M \times 10^4)$$

where

B is the quantity of boron expressed as a percentage of the fertiliser;

x_s is the concentration (μg/ml) in the test solution (6-2), with or without correction;

x_b is the concentration (μg/ml) in the blank (7-1);

V is the volume in ml of extract obtained in accordance with Method 9.1 or 9.2;

D is the factor corresponding to the dilution carried out in 6-2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: if (a_1) and (a_2) are successive aliquot portions and (v_1) and (v_2) are the volumes corresponding to their respective dilutions, the dilution factor D is given by:

$$D = (V1/a1) \times (V2/a2)$$

Method 9.6
Determination of cobalt in fertiliser extracts by atomic absorption spectrometry

1- Scope

This Method describes a procedure for determining cobalt in fertilizer extracts.

2- Field of application

This Procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble cobalt is required by Annex I E of this Regulation.

3- Principle

After suitable treatment and dilution of the extracts, the cobalt content is determined by atomic absorption spectrometry.

4- Reagents

4-1 Hydrochloric acid solution, about 6 mol/l

See Method 9.4 (4.1).

4-2   Hydrochloric acid solution, about 0,5 mol/l
       See Method 9.4 (4.2).
4-3   Lanthanum salt solutions (10 g of La per litre)
       See Method 9.4 (4.3).
4-4   Cobalt calibration solutions
4-4-1 Cobalt stock solution (1 000 µg/ml)
       In a 250 ml beaker, weigh to the nearest 0,1 mg, 1 g of cobalt, add 25 ml of 6 mol/l hydrochloric acid (4-1) and heat on a hotplate until the cobalt is completely dissolved. When cool, transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.
4-4-2 Cobalt working solution (100 µg/ml)
       Place 10 ml of the stock solution (4-4-1) in a 100 ml volumetric flask.
       Make up to volume with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

5- Apparatus

Atomic absorption spectrometer: see Method 9.4 (5). The instrument must be equipped with a source of rays characteristic of cobalt (240,7 nm). The spectrometer must allow background correction to be made.

6- Preparation of the solution to be analysed

6-1   Cobalt extract solution
       See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.
6-2   Preparation of the test solution
       See Method 9.4 (6-2). The test solution must contain 10 % (v/v) of a lanthanum salt solution (4-3).

7- Procedure

7-1   Preparation of blank solution
       See Method 9.4 (7-1). The blank must contain 10 % (v/v) of the lanthanum salt solution used in 6-2.
7-2   Preparation of calibration solutions
       See Method 9.4 (7-2).
       For an optimum determination range of 0 to 5 µg/ml of cobalt, place 0, 0,5, 1, 2, 3, 4 and 5 ml respectively of working solution (4-4-2) in a series of 100 ml volumetric flasks. If necessary adjust the hydrochloric acid concentration as closely as possible to that of the test solution. Add to each flask 10 ml of the lanthanum salt solution used in 6-2. Make up to 100 ml with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly. These solutions contain 0, 0,5, 1, 2, 3, 4 and 5 µg/ml respectively of cobalt.
7-3   Determination
       See Method 9.4 (7-3). Prepare the spectrometer (5) for measurement at a wavelength of 240,7 nm.

8- Expression of results

See Method 9.4 (8).
The percentage of cobalt in the fertiliser is given by:
$$Co\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$
If Method 9.3 is used:
$$Co\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$
where
Co is the quantity of cobalt expressed as a percentage of the fertiliser;
x_s is the concentration in µg/ml of the test solution (6.2);
x_b is the concentration in µg/ml of the blank solution (7.1);
V is the volume in ml of extract obtained in accordance with Method 9.1 or 9.2;
D is the factor corresponding to the dilution carried out in 6.2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: if (a_1), (a_2), (a_3),.,.,., (ai) and (a) are aliquot portions and (v_1), (v_2), (v_3),.,.,., (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D is given by:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times.\times.\times.\times.\times (Vi/ai) \times (100/a)$$

Method 9.7

Determination of copper in fertiliser extracts by atomic absorption spectrometry

1- Scope

This Method describes a procedure for determining copper in fertilizer extracts.

2- Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble copper is required by Annex I E to this Regulation.

3- Principle

After suitable treatment and dilution of the extracts, the copper content is determined by atomic absorption spectrometry.

4- Reagents

4-1 Hydrochloric acid solution, about 6 mol/l
See Method 9.4 (4-1).

4-2 Hydrochloric acid solution, about 0,5 mol/l
See Method 9.4 (4-2).

4-3 Hydrogen peroxide solution (30 % H_2O_2, d_{20} = 1,11 g/ml), free from micro nutrients

4-4 Copper calibration solutions

4-4-1 Copper stock solution (1 000 μg/ml)
In a 250 ml beaker, weigh to the nearest 0,1 mg, 1 g of copper, add 25 ml of 6 mol/l hydrochloric acid (4-1), add 5 ml hydrogen peroxide solution (4-3) and heat on a hotplate until the copper is completely dissolved. Transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.

4-4-2 Copper working solution (100 μg/ml)
Place 20 ml of the stock solution (4-4-1) in a 200 ml volumetric flask. Make up to volume with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

5- Apparatus

Spectrometer equipped for atomic absorption: see Method 9.4 (5). The instrument must be fitted with a source of rays characteristics of copper (324,8 nm).

6- Preparation of the solution to be analysed

6-1 Copper extract solution
See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2 Preparation of the test solution
See Method 9.4 (6.2).

7- Procedure

7-1 Preparation of blank solution
See Method 9.4 (7.1).

7-2 Preparation of calibration solutions
See Method 9.4 (7.2).
For an optimum determination range of 0 to 5 μg/ml of copper, place 0, 0,5, 1, 2, 3, 4 and 5 ml respectively of working solution (4-4-2) in a series of 100 ml volumetric flasks. If necessary adjust the hydrochloric acid concentration as closely as possible to that of the test solution (6-2). Make up to 100 ml with 0,5 mol/l hydrochloric acid

solution (4-2) and mix thoroughly. These solutions contain 0, 0,5, 1, 2, 3, 4 and 5 µg/ml respectively of copper.

7-3 Determination

See Method 9.4 (7-3). Prepare the spectrometer (5) for measurement at a wavelength of 324,8 nm.

8- **Expression of results**

See Method 9.4 (8).

The percentage of copper in the fertiliser is given by:

$$Cu\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$

If Method 9.3 is used:

$$Cu\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$

where

Cu is the quantity of copper expressed as a percentage of the fertiliser;

xs is the concentration in µg/ml of the test solution (6-2);

xb is the concentration in µg/ml of the blank solution (7-1);

V is the volume in ml of extract obtained in accordance with Method 9.1 or 9.2;

D is the factor corresponding to the dilution carried out in 6.2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: if (a_1), (a_2), (a_3),.,.,., (ai) and (a)

are aliquot portions and (v_1), (v_2), (v_3),.,.,., (vi) and (100) are the

volumes in ml corresponding to their respective dilutions, the

dilution factor D is given by:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times . \times . \times . \times (Vi/ai) \times (100/a)$$

Method 9.8

Determination of iron in fertiliser extracts by atomic absorption spectrometry

1- **Scope**

This Method describes a procedure for determining iron in fertilizer extracts.

2- **Field of application**

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble iron is required by Annex 1E of this Regulation.

3- **Principle**

After suitable treatment and dilution of the extracts, the iron content is determined by atomic absorption spectrometry.

4- **Reagents**

4-1 Hydrochloric acid solution, about 6 mol/l

See Method 9.4 (4-1).

4-2 Hydrochloric acid solution, about 0,5 mol/l

See Method 9.4 (4-2).

4-3 Hydrogen peroxide solution (30 % H_2O_2, d_{20} = 1,11 g/ml), free from micro-nutrients

4-4 Lanthanum salt solutions (10 g of La per litre)

See Method 9.4 (4-3).

4-5 Iron calibration solutions

4-5-1 Iron stock solution (1 000 µg/ml)

In a 500 ml beaker, weigh to the nearest 0,1 mg, 1 g of iron wire, add 200 ml of 6 mol/l hydrochloric acid (4-1) and 15 ml of hydrogen peroxide solution (4-3). Heat on a hotplate until the iron is completely dissolved. When cool, transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.

4-5-2 Iron working solution (100 μg/ml)

Place 20 ml of the stock solution (4-5-1) in a 200 ml volumetric flask. Make up to volume with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

5- Apparatus

Atomic absorption spectrometer: see Method 9.4 (5). The instrument must be fitted with a source of rays characteristic of iron (248,3 nm).

6- Preparation of the solution to be analysed

6-1 Iron extract solution

See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2 Preparation of the test solution

See Method 9.4 (6-2). The test solution must contain 10 % (v/v) of a lanthanum salt solution.

7- Procedure

7-1 Preparation of blank solution

See Method 9.4 (7-1). The test solution must contain 10 % (v/v) of the lanthanum salt solution used in 6-2.

7-2 Preparation of calibration solutions

See Method 9.4 (7-2).

For an optimum determination range of 0 to 10 μg/ml of iron, place 0, 2, 4, 6, 8 and 10 ml respectively of working solution (4-5-2) in a series of 100 ml volumetric flasks. If necessary adjust the hydrochloric acid concentration as closely as possible to that of the test solution. Add 10 ml of the lanthanum salt solution used in 6-2. Make up to volume with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly. These solutions contain 0, 2, 4, 6, 8 and 10 μg/ml respectively of iron.

7-3 Determination

See Method 9.4 (7-3). Prepare the spectrometer (5) for measurement at a wavelength of 248,3 nm.

8- Expression of results

See Method 9.4 (8).

The percentage of iron in the fertiliser is given by:

$$Fe\% = ((X_s - X_b) \times V \times D)/(M \times 10^4)$$

If Method 9.3 is used:

$$Fe\% = ((X_s - X_b) \times V \times 2D)/(M \times 10^4)$$

where

Fe is the quantity of iron expressed as a percentage of the fertiliser;

x_s is the concentration in μg/ml of the test solution (6-2);

x_b is the concentration in μg/ml of the blank solution (7-1);

V is the volume in ml of extract obtained in accordance with Method 9.1 or 9.2;

D is the factor corresponding to the dilution carried out in 6-2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: if (a_1), (a_2), (a_3),.,.,., (ai) and (a) are aliquot portions and (v_1), (v_2), (v_3),.,.,., (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D is given by:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times.\times.\times.\times.\times (Vi/ai) \times (100/a)$$

Method 9.9

Determination of manganese in fertiliser extracts by atomic absorption spectrometry

1- Scope

This Method describes a procedure for determining manganese in fertiliser extracts.

2- Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble manganese is required by Annex I E of this Regulation.

3- Principle

After suitable treatment and dilution of the extracts, the manganese level is determined by atomic absorption spectrometry.

4- Reagents

4-1   Hydrochloric acid solution, about 6 mol/l
See Method 9.4 (4-1).

4-2   Hydrochloric acid solution, about 0,5 mol/l
See Method 9.4 (4-2).

4-3   Lanthanum salt solutions (10 g of La per litre)
See Method 9.4 (4-3).

4-4   Manganese calibration solutions

4-4-1   Manganese stock solution (1 000 μg/ml)
In a 250 ml beaker, weigh to the nearest 0,1 mg, 1 g of manganese, add 25 ml of 6 mol/l hydrochloric acid (4-1). Heat on a hotplate until the manganese is completely dissolved. When cool, transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.

4-4-2   Manganese working solution (100 μg/ml)
Dilute 20 ml of the stock solution (4-4-1) in the 0,5 mol/l hydrochloric acid solution (4-2) in a 200 ml volumetric flask. Make up to volume with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

5- Apparatus

Atomic absorption spectrometer: see Method 9.4 (5). The instrument must be fitted with a source of lines characteristic of manganese (279,6 nm).

6- Preparation of the solution to be analysed

6-1   Manganese extract solution
See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2   Preparation of the test solution
See Method 9.4 (6-2). The test solution must contain 10 % by volume of lanthanum salt solution (4-3).

7- Procedure

7-1   Preparation of blank solution
See Method 9.4 (7-1). The test solution must contain 10 % by volume of the lanthanum salt solution used in 6-2.

7-2   Preparation of calibration solutions
See Method 9.4 (7-2).
For an optimum determination range of 0 to 5 μg/ml of manganese, place 0, 0,5, 1, 2, 3, 4 and 5 ml respectively of working solution (4-4-2) in a series of 100 ml volumetric flasks. Where necessary adjust the hydrochloric acid concentration to bring it as close as possible to that of the test solution. To each flask, add 10 ml of the lanthanum salt solution used in 6-2. Make up to 100 ml with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly. These solutions contain 0, 0,5, 1, 2, 3, 4 and 5 μg/ml respectively of manganese.

7-3   Determination
See Method 9.4 (7-3). Prepare the spectrometer (5) for measurement at a wavelength of 279,6 nm.

8- Expression of results

See Method 9.4 (8).

The percentage of manganese in the fertiliser is as follows:

$$Mn\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$

If Method 9.3 is used:

$$Mn\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$

where

Mn is the quantity of manganese expressed as a percentage of the fertiliser;

x_s is the concentration in μg/ml of the test solution (6-2);

x_b is the concentration in μg/ml of the blank solution (7-1);

V is the volume in ml of extract obtained in accordance with Method 9.1 or 9.2;

D is the factor corresponding to the dilution carried out in 6-2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: if (a_1), (a_2), (a_3),.,.,., (ai) and (a) are aliquot portions and (v_1), (v_2), (v_3),.,.,., (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D will be equal to:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times.\times.\times.\times.\times (Vi/ai) \times (100/a)$$

Method 9.10

Determination of molybdenum in fertiliser extracts by spectrometry of a complex with ammonium thiocyanate

1- **Scope**

This Method describes a procedure for determining molybdenum in fertiliser extracts.

2- **Field of application**

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble molybdenum is required by Annex I E to this Regulation.

3- **Principle**

Molybdenum (V) forms a complex $[MoO(SCN)_5]^-$ in an acid medium with SCN- ions.

The complex is extracted with n-butyl acetate. Interfering ions such as those of iron remain in the aqueous phase. The yellow-orange colour is determined by molecular absorption sectrometry at 470 nm.

4- **Reagents**

4-1 Dilute hydrochloric acid solution (HCl), about 6 mol/l

See Method 9.4 (4-1).

4-2 Copper solution (70 mg/l) in 1,5 mol/l hydrochloric acid

Dissolve 275 mg of copper sulphate (CuSO4.5H2O) weighed to within 0,1 mg in 250 ml of the 6 mol/l hydrochloric acid solution (4-1) in a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.

4-3 Ascorbic acid solution (50 g/l)

Dissolve 50 g of ascorbic acid $(C_6H_8O_6)$ in water in a 1 000 ml volumetric flask. Make up to volume with water, mix thoroughly and keep in a refrigerator.

4-4 n-butyl acetate

4-5 Ammonium thiocyanate solution, 0,2 mol/l

Dissolve 15,224 g of NH4SCN in water in a 1 000 ml volumetric flask. Make up to volume with water; mix thoroughly and store in a dark-coloured bottle.

4-6 Stannous chloride solution (50 g/l) in 2 mol/l hydrochloric acid

This solution must be perfectly clear and prepared immediately before use. Very pure stannous chloride must be used otherwise the solution will not be clear.

To prepare 100 ml of solution, dissolve 5 g of (SnCl$_2$.2H2O) in 35 ml of 6 mol/l HCl solution (4.1). Add 10 ml of the copper solution (4.2). Make up to volume with water and mix thoroughly.

4-7 Molybdenum calibration solutions

4-7-1 Molybdenum stock solution (500 μg/ml)

Dissolve 0,920 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}$ $4H_2O$] weighed to within 0,1 mg in the 6 mol/l hydrochloric acid (4-1) in a 1 000 ml volumetric flask. Make up to volume with that solution and mix thoroughly.

4-7-2 Molybdenum intermediate solution (25 μg/ml)

Place 25 ml of the stock solution (4-7-1) in a 500 ml volumetric flask. Make up to volume with 6 mol/l hydrochloric acid (4-1) and mix thoroughly.

4-7-3 Molybdenum working solution (2,5 μg/ml)

Place 10 ml of the intermediate solution (4-7-2) in a 100 ml volumetric flask. Make up to volume with 6 mol/l hydrochloric acid (4-1) and mix thoroughly.

5- Apparatus

5-1 Spectrometer fitted for molecular absorption with cuvettes having a 20 mm optical path and set to a wavelength of 470 nm

5-2 200 or 250 ml separating funnels

6- Preparation of the solution to be analysed

6-1 Molybdenum extract solution

See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2 Preparation of the test solution

Dilute an aliquot portion of the extract (6-1) with 6 mol/l hydrochloric acid solution (4-1) so as to obtain an appropriate molybdenum concentration. Let D be the dilution factor.

Take an aliquot portion (a) from the extract solution containing 1 to 12 μg molybdenum and place it in the separating funnel (5-2). Make up to 50 ml with the 6 mol/l hydrochloric acid solution (4-1).

7- Procedure

7-1 Preparation of the blank solution

Prepare a blank solution by repeating the whole procedure from the extraction stage, omitting only the test sample of fertiliser.

7-2 Preparation of the series of calibration solutions

Prepare a series of at least six calibration solutions of increasing concentration corresponding to the optimum response range of the spectrometer.

For the interval 0-12,5 μg molybdenum, place 0, 1, 2, 3, 4 and 5 ml respectively of working solution (4-7-3) in the separating funnels (5-2). Make up to 50 ml with 6 mol/l hydrochloric acid (4-1). The funnels contain respectively 0, 2,5, 5, 7,5, 10 and 12,5 μg molybdenum.

7-3 Development and separation of the complex

To each separating funnel (6.2, 7.1 and 7.2), add in the following order:

−   10 ml of the copper solution (4-2)

−   20 ml of the ascorbic acid solution (4-3);

mix thoroughly and wait for two or three minutes. Then add:

−   10 ml of n-butyl acetate (4-4), using a precision pipette

−   20 ml of the thiocyanate solution (4-5).

Shake for one minute to extract the complex in the organic phase; allow to precipitate; after the separation of the two phases, draw off the entire aqueous phase and discard it; then wash the organic phase with:

−   10 ml of the stannous chloride solution (4-6).

Shake for one minute. Allow to precipitate and draw off the entire aqueous phase. Collect the organic phase in a test tube; this will make it possible to collect the drops of water in suspension.

7-4 Determination

Measure the absorbencies of the solutions obtained at 7-3 at a wavelength of 470 nm using the 0 μg/ml molybdenum calibration solution (7-2) as a reference.

8- Expression of results

Construct the calibration curve by plotting the corresponding masses of molybdenum in the calibration solutions (7-2) expressed in µg along the abscissa and the corresponding values of the absorbencies (7-4) given by the spectrometer reading along the ordinate.

From this curve determine the mass of molybdenum in the test solution (6-2) and the blank solution (7-1). These masses are designated (x_s) and (x_b) respectively.

The percentage of molybdenum in the fertiliser is:

$$Mo\% = ((Xs - Xb) \times V/a \times D)/(M \times 10^4)$$

If Method 9.3 is used:

$$Mo\% = ((Xs - Xb) \times V/a \times 2D)/(M \times 10^4)$$

where

Mo is the quantity of molybdenum expressed as a percentage of the fertiliser;

a is the volume in ml of the aliquot taken from the last dilute solution (6-2);

x_s is the Mo mass in µg in the test solution (6-2);

x_b is the Mo mass in µg in the blank solution (7-1) the volume of which corresponds to the volume (a) of the aliquot of the test solution (6-2);

V is the volume in ml of extract solution obtained in accordance with Method 9.1 or 9.2;

D is the factor corresponding to the dilution performed in 6-2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: where (a_1), (a_2) are successive aliquot portions and (v_1), (v_2) are the volumes corresponding to their respective dilutions, the dilution factor D will be:

$$D = (V1/a1) \times (V2/a2)$$

Method 9.11
Determination of zinc in fertiliser extracts by atomic absorption spectrometry

1- Scope

This Method describes a procedure for determining zinc in fertilizer extracts.

2- Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 9.1 and 9.2 for which a declaration of total and/or water-soluble zinc is required by Annex I E to this Regulation.

3- Principle

After suitable treatment and dilution of the extracts, the zinc level is determined by atomic absorption spectrometry.

4- Reagents

4-1 Hydrochloric acid solution, about 6 mol/l
  See Method 9.4 (4-1).

4-2 Hydrochloric acid solution, about 0,5 mol/l
  See Method 9.4 (4-2).

4-3 Lanthanum salt solutions (10 g of La per litre)
  See Method 9.4 (4-3).

4-4 Zinc calibration solutions

  4-4-1 Zinc stock solution (1 000 µg/ml)
    In a 1 000 ml volumetric flask, dissolve 1 g of zinc powder or flakes weighed to within 0,1 mg in 25 ml of 6 mol/l hydrochloric acid (4-1).
    When completely dissolved, make up to volume with water and mix thoroughly.

  4-4-2 Zinc working solution (100 µg/ml)
    In a 200 ml volumetric flask, dilute 20 ml of the stock solution (4-4-1) in 0,5 mol/l hydrochloric acid solution (4-2). Make up to volume with the 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

5- Apparatus

Atomic absorption spectrometer: see Method 9.4 (5). The instrument must be fitted with a source of lines characteristic of zinc (213,8 nm), the spectrometer must allow background correction to be made.

6- Preparation of the solution to be analysed

6-1 Zinc extract solution

See Methods 9.1 and/or 9.2 and, if appropriate, 9.3.

6-2 Preparation of the test solution

See Method 9.4 (6-2). The test solution must contain 10 % by volume of lanthanum salt solution (4-3).

7- Procedure

7-1 Preparation of blank solution

See Method 9.4 (7-1). The test solution must contain 10 % by volume of the lanthanum salt solution used in 6-2.

7-2 Preparation of calibration solutions

See Method 9.4 (7-2).

For an optimum interval of 0 to 5 μg/ml of zinc, place 0, 0,5, 1, 2, 3, 4 and 5 ml respectively of working solution (4-4-2) in a series of 100 ml volumetric flasks. Where necessary adjust the hydrochloric acid concentration to bring it as close as possible to that of the test solution. To each flask, add 10 ml of the lanthanum salt solution used in 6-2. Make up to 100 ml with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly. These solutions contain 0, 0,5, 1, 2, 3, 4 and 5 μg/ml respectively of zinc.

7-3 Determination

See Method 9.4 (7-3). Prepare the spectrometer (5) for measurement at a wavelength of 213,8 nm.

8- Expression of results

See Method 9.4 (8).

The percentage of zinc in the fertiliser is as follows:

$$Zn\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$

If Method 9.3 is used:

$$Zn\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$

where

Zn is the quantity of zinc expressed as a percentage of the fertiliser;

x_s is the concentration in μg/ml of the test solution (6-2);

x_b is the concentration in μg/ml of the blank solution (7-1);

V is the volume in ml of extract obtained in accordance with Method 9.1 or 9.2;

D is the factor corresponding to the dilution carried out in 6-2;

M is the mass in grams of the test sample taken in accordance with Method 9.1 or 9.2.

Calculation of the dilution factor D: if (a_1), (a_2), (a_3),.,.,., (a_i) and (a) are aliquot portions and (v_1), (v_2), (v_3),.,.,., (v_i) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D will be equal to:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times.\times.\times.\times.\times (Vi/ai) \times (100/a)$$

<div align="center">

Methods 10

Micro-nutrients at a concentration greater than 10 %

Method 10.1

Extraction of total micro-nutrients

</div>

1- Scope

This Method defines the procedure for extracting the following micro-nutrients: total boron, total cobalt, total copper, total iron, total manganese, total molybdenum and total zinc. The

aim is to carry out the minimum number of extractions, making use wherever possible of the same extract to determine the total level of each of the micro-nutrients listed above.

2-　　Field of application

This procedure concerns Community fertilisers covered by Annex I E to this Regulation containing one or more of the following micro-nutrients: boron, cobalt, copper, iron, manganese, molybdenum and zinc. It is applicable to each micro-nutrient the declared content of which is more than 10 %.

3-　　Principle

Dissolution in boiling dilute hydrochloric acid.

N o t e

The extraction is empirical and may not be quantitative depending on the product or the other constituents of the fertiliser. In particular, in the case of certain manganese oxides, the quantity extracted may be substantially smaller than the total quantity of manganese which the product contains. It is the responsibility of the fertiliser manufacturers

to ensure that the declared content actually corresponds to the quantity extracted under the conditions pertaining to the method.

4-　　Reagents

4-1　　Dilute hydrochloric acid (HCl) solution, about 6 mol/l

　　　　Mix 1 volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 1 volume of water.

4-2　　Concentrated ammonia solution (NH_4OH, d_{20} = 0,9 g/ml)

5-　　Apparatus

5-1　　Electric hotplate with variable temperature control

5-2　　pH meter

　　　　N o t e

　　　　Where the boron content of an extract is to be determined, do not use borosilicate glassware. As the Method involves boiling, teflon or silica is preferable. Rinse the glassware thoroughly if it has been washed in detergents containing borates.

6-　　Preparation of the sample

See Method 1.

7-　　Procedure

7-1　　Test sample

　　　　Take a quantity of fertiliser weighing 1 or 2 g depending on the declared content of element in the product. The following table shall be used to obtain a final solution which, after appropriate dilution, will be within the measuring range for each method. Samples should be weighed to within 1 mg.

Declared content of micro-nutrient in the fertiliser (%)	> 10 < 25	≥ 25
Mass of test sample (g)	2	1
Mass of element in the sample (mg)	> 200 < 500	≥ 250
Volume of extract V (ml)	500	500
Concentration of element in extract (mg/l)	> 400 < 1 000	≥ 500

　　　　Place the sample in a 250 ml beaker.

7-2　　Preparation of the solution

　　　　If necessary moisten the sample with a little water, add 10 ml of dilute hydrochloric acid (4-1) per gram of fertiliser carefully, in small amounts, then add about 50 ml of

water. Cover the beaker with a watch glass and mix. Bring to the boil on the hotplate and boil for 30 minutes. Allow to cool, stirring occasionally. Transfer quantitatively to a 500 ml volumetric flask. Make up to volume with water and mix thoroughly. Filter through a dry filter into a dry container. Discard the first portion. The extract must be perfectly clear.

It is recommended that the determination be carried out without delay on aliquot portions of the clear filtrate, if not the containers should be stoppered.

N o t e

Extracts in which the boron content has to be determined: Adjust the pH to between 4 and 6 with concentrated ammonia (4-2).

8- Determination

The determination of each micro-nutrient is to be carried out on the aliquot portions indicated in the Method for each individual micro-nutrient.

Methods 10.5, 10.6, 10.7, 10.9 and 10.10 cannot be used to determine elements present in a chelated or complexed form. In such cases Method 10.3 must be used prior to the determination.

In the case of determination by AAS (Methods 10.8 and 10.11) such treatment may not be necessary.

Method 10.2
Extraction of water-soluble micro-nutrients

1- Scope

This Method defines the procedure for extracting water-soluble forms of the following micro-nutrients: boron, cobalt, copper, iron, manganese, molybdenum and zinc. The aim is to carry out the minimum number of extractions, making use wherever possible of the same extract to determine the level of each of the micro-nutrients listed above.

2- Field of application

This Procedure concerns Community fertilisers covered by Annex I E to this Regulation containing one or more of the following micro-nutrients: boron, cobalt, copper, iron, manganese, molybdenum and zinc. It is applicable to each micro-nutrient the declared content of which is more than 10 %.

3- Principle

The micro-nutrients are extracted by shaking the fertiliser in water at 20 °C (± 2) °C.

N o t e

The extraction is empirical and may or may not be quantitative.

4- Reagents

4-1   Dilute hydrochloric acid (HCl) solution, about 6 mol/l

Mix 1 volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 1 volume of water.

5- Apparatus

5-1   Rotary shaker set at about 35 to 40 rpm

N o t e

Where the boron content of the extract is to be determined, do not use borosilicate glassware. Teflon or silica is preferable for this extraction. Rinse the glassware thoroughly if it has been washed in detergents containing borates.

6- Preparation of the sample

See Method 1.

7- Procedure

7-1   Test sample

Take a quantity of fertiliser weighing 1 or 2 g depending on the declared content of the product. The following table shall be used to obtain a final solution which, after appropriate dilution, will be within the measuring range for each method. The samples should be weighed to within 1 mg.

Declared content of micro-nutrient in the fertiliser (%)	> 10 < 25	≥ 25
Mass of test sample (g)	2	1
Mass of element in the sample (mg)	> 200 < 500	≥ 250
Volume of extract V (ml)	500	500
Concentration of element in extract (mg/l)	> 400 < 1 000	≥ 500

Place the sample in a 500 ml flask.

7-2 Preparation of the solution

Add about 400 ml of water.

Stopper the flask well. Shake vigorously by hand to disperse the sample, then place the flask on the shaker and shake for 30 minutes.

Make up to volume with water and mix thoroughly.

7-3 Preparation of the test solution

Filter immediately into a clean, dry flask. Stopper the flask. Carry out the determination immediately after filtering.

N o t e

If the filtrate gradually becomes cloudy, make another extraction following 7-1 and 7-2 in a flask of volume V_e. Filter into a calibrated flask of volume W which has previously been dried and has received 5 ml of dilute hydrochloric acid (4-1). Stop the filtration at the exact moment when the calibration mark is reached. Mix thoroughly.

Under these conditions the value of V in the expression of results is:

$$V = Ve \times W/(W - 5)$$

The dilutions in the expression of results depend on this value of V.

8- Determination

The determination of each micro-nutrient is carried out on the aliquot portions indicated in the Method for each individual micro-nutrient.

Methods 10.5, 10.6, 10.7, 10.9 and 10.10 cannot be used to determine elements present in a chelated or complexed form. In such cases Method 10.3 must be used prior to the determination.

In the case of determination by AAS (Methods 10.8 and 10.11) such treatment may not be necessary.

Method 10.3
Removal of organic compounds from fertiliser extracts

1- Scope

This Method defines a procedure for removing organic compounds from fertiliser extracts.

2- Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 10.1 and 10.2 for which a declaration of total and/or water-soluble element is required by Annex I E to this Regulation.

N o t e

The presence of small quantities of organic matter usually does not affect determination by means of atomic absorption spectrometry.

3-Principle

The organic compounds in an aliquot portion of the extract are oxidised with hydrogen peroxide.

4-   Reagents

4-1   Dilute hydrochloric acid (HCl) solution, about 0,5 mol/l

Mix 1 volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 20 volumes of water.

4-2   Hydrogen peroxide solution (30 % H_2O_2, d_{20} = 1,11 g/ml), free from micro-nutrients

5-   Apparatus

Electric hotplate with variable temperature control.

6-   Procedure

Take 25 ml of the extract solution obtained by Method 10.1 or Method 10.2 and place in a 100 ml beaker. In the case of Method 10.2, add 5 ml of the dilute hydrochloric acid solution (4-1). Then add 5 ml of the hydrogen peroxide solution (4-2). Cover with a watch glass. Allow oxidation to occur at room temperature for about one hour, then bring gradually to boiling and boil for half an hour. If necessary, add a further 5 ml of the hydrogen peroxide to the solution once it has cooled. Then boil to remove the excess hydrogen peroxide. Allow to cool and transfer quantitatively to a 50 ml volumetric flask and make up to volume. Filter where necessary.

Account should be taken of this dilution when taking aliquot portions and calculating the percentage of micro-nutrient in the product.

Method 10.4

Determination of micro-nutrients in fertiliser extracts by atomic absorption spectrometry
(general procedure)

1-   Scope

This document defines a general procedure for determining the levels of iron and zinc in fertiliser extracts by atomic absorption spectrometry.

2-   Field of application

This procedure is applicable to analysing samples of fertilizers extracted by Methods 10.1 and 10.2 for which a declaration of total and/or water-soluble iron or zinc is required by Annex I E to this Regulation.

Adaptations of this procedure for the various micro-nutrients are detailed in the methods defined specifically for each element.

N o t e

In most cases the presence of small quantities of organic matter will not affect determinations by atomic absorption spectrometry.

3-   Principle

After the extract has been treated where necessary to reduce or eliminate interfering chemical species, the extract is diluted so that its concentration is in the optimum range of the spectrometer at a wavelength suitable for the micro-nutrient to be determined.

4-   Reagents

4-1   Dilute hydrochloric acid solution (HCl), about 6 mol/l

Mix one volume of hydrochloric acid (d_{20} = 1,18 g/ml) with one volume of water.

4-2   Dilute hydrochloric acid solution (HCl), about 0,5 mol/l

Mix one volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 20 volumes of water.

4-3   Lanthanum salt solutions (10 g of La per litre)

This reagent is used for determinations of iron and zinc. It can be prepared either:

(a)   with lanthanum oxide dissolved in hydrochloric acid (4-1). Place 11,73 g of lanthanum oxide (La_2O_3) in 150 ml of water in a one litre volumetric flask and add 120 ml of 6 mol/l hydrochloric acid (4-1). Allow to dissolve and then make up to 1 litre with water and mix thoroughly. This solution is approximately 0,5 mol/l in hydrochloric acid; or

(b)   with solutions of lanthanum chloride, sulphate or nitrate. Dissolve 26,7 g of lanthanum chloride heptahydrate ($LaCl_3.7H_2O$) or 31,2 g of lanthanum

nitrate hexahydrate [La(NO$_3$)$_3$.6H$_2$O] or 26,2 g of lanthanum sulphate nonahydrate [La$_2$(SO$_4$)$_3$.9H$_2$O] in 150 ml of water, then add 85 ml of 6 mol/l hydrochloric acid (4-1). Allow to dissolve and then make up to 1 litre with water. Mix thoroughly. This solution is approximately 0,5 mol/l in hydrochloric acid.

    4-4   Calibration solutions

For the preparation of these, see the individual determination Method for each micro-nutrient.

5- Apparatus

Atomic absorption spectrometer fitted with sources emitting radiation characteristic of the micro-nutrients to be determined.

The analyst must follow the manufacturer's instructions and be familiar with the apparatus. The apparatus must allow background correction so that it can be used whenever necessary (e.g. Zn). The gases to be used are air and acetylene.

6- Preparation of the solution to be analysed

    6-1   Preparation of extract solutions containing the elements to be determined

See Methods 10.1 and/or 10.2 and, if appropriate, 10.3.

    6-2   Treatment of the test solution

Dilute an aliquot portion of the extract obtained by Method 10.1, 10.2 or 10.3 with water and/or hydrochloric acid (4-1) or (4-2) so as to obtain, in the final solution for measurement, a concentration of the element to be determined that is appropriate to the calibration range used (7-2) and a hydrochloric acid concentration of at least 0,5 mol/l and not more than 2,5 mol/l. This operation may require one or more successive dilutions.

The final solution has to be obtained by placing an aliquot portion of the diluted extract in a 100 ml volumetric flask. Let the volume of this aliquot portion be (a) ml. Add 10 ml of the lanthanum salt solution (4-3). Make up to volume with the 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly. Let D be the dilution factor.

7- Procedure

    7-1   Preparation of a blank solution

Prepare a blank solution by repeating the whole procedure from the extraction stage, omitting only the test sample of fertiliser.

    7-2   Preparation of calibration solutions

From the working calibration solution prepared using the Method given for each individual micro-nutrient, prepare in 100 ml volumetric flasks a series of at least five calibration solutions of increasing concentration within the optimum measuring range of the spectrometer. If necessary, adjust the concentration of hydrochloric acid to bring it as close as possible to that of the diluted test solution (6-2). When determining iron or zinc, add 10 ml of the same lanthanum salt solution (4-3) as used in 6-2. Make up to volume with the 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

    7-3   Determination

Prepare the spectrometer (5) for the determination and adjust to the wavelength given in the Method for the individual micro-nutrient concerned.

Spray three times in succession the calibration solutions (7-2), the test solution (6-2) and the blank solution (7-1), noting each result and flushing the instrument with distilled water between individual sprayings.

Construct the calibration curve by plotting the average spectrometer reading for each calibration solution (7-2) along the ordinate and the corresponding concentration of the element, expressed in μg/ml, along the abscissa.

From this curve, determine the concentrations of the relevant micro-nutrient in the test solution x_s (6-2) and in the blank solution x_b(7-1), expressing these concentrations in µg per ml.

8-   Expression of results

The percentage of micro-nutrient (E) in the fertiliser is given by:

$$E\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$

If Method 10.3 has been used:

$$E\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$

Where

E is the amount of the micro-nutrient determined, expressed as a percentage of the fertiliser;

x_s is the concentration of the test solution (6.2), in µg/ml;

x_b is the concentration of the blank solution (7.1), in µg/ml;

V is the volume of the extract obtained by Method 10.1 or 10.2, in ml;

D is the factor corresponding to the dilution carried out in 6.2;

M is the mass of the test sample taken in accordance with Method 10.1 or 10.2, in grams.

Calculation of dilution factor D:

If (a_1), (a_2), (a_3),.,.,., (ai) and (a) are the aliquot portions and (v_1), (v_2), (v_3),.,.,., (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D will be equal to:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times.\times.\times.\times.\times (Vi/ai) \times (100/a)$$

Method 10.5

Determination of boron in fertiliser extracts by means of acidimetric titration

1-   Scope

This Method defines a procedure for determining the boron content of fertiliser extracts.

2-   Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 or Method 10.2 and for which a declaration of total and/or water-soluble boron is required by Annex I E to this Regulation.

3-   Principle

A mannitoboric complex is formed by the following reaction of the borate with mannitol:

$$C_6H_8(OH)_6 + H_3BO_3C_6H_{15}O_8B + H_2O$$

The complex is titrated with sodium hydroxide solution to a pH of 6,3.

4-   Reagents

4-1   Methyl red indicator solution

Dissolve 0,1 g of methyl red ($C_{15}H_{15}N_3O_2$) in 50 ml of ethanol (95 % in a 100 ml volumetric flask). Make up the volume to 100 ml with water. Mix thoroughly.

4-2   Diluted hydrochloric acid solution, about 0,5 mol

Mix 1 volume of hydrochloric acid HCl ($d_{20} = 1,18$ g/ml) with 20 volumes of water.

4-3   Sodium hydroxide solution, about 0,5 mol/l

Must be free of carbon dioxide. Dissolve 20 g of sodium hydroxide (NaOH) in pellet form in a 1 litre volumetric flask containing about 800 ml of boiled water. When the solution has cooled, make up to 1 000 ml with boiled water and mix thoroughly.

4-4   Standard sodium hydroxide solution, about 0,025 mol/l

Must be free of carbon dioxide. Dilute the 0,5 mol/l sodium hydroxide solution (4-3) 20 times with boiled water and mix thoroughly. The value of the solution expressed as boron (B) is to be determined (see Paragraph 9).

4-5   Boron calibration solution (100 µg/ml B)

Dissolve 0,5719 g of boric acid (H_3BO_3), weighed to the nearest 0,1 mg, in water in a 1,000 ml volumetric flask. Make up to volume with water and mix thoroughly. Transfer to a plastic bottle for storage in a refrigerator.

4-6   D-mannitol ($C_6H_{14}O_6$) powder

4-7   Sodium chloride (NaCl)

5-   Apparatus

5-1   pH meter with glass electrode

5-2   Magnetic stirrer

5-3   400 ml beaker with teflon rod

6-   Preparation of the solution to be analysed

6-1   Preparation of the boron solution

         See Methods 10.1, 10.2 and, where appropriate, 10.3.

7-   Procedure

7-1   Test

Place in a 400 ml beaker (5-3) an aliquot (a) of the extract (6-1) containing 2 to 4 mg B. Add 150 ml of water.

Add several drops of the methyl red indicator solution (4-1).

In the case of extraction with Method 10.2, acidify by adding 0,5 mol/l hydrochloric acid (4-2) up to the point of change of the indicator solution, then add a further 0,5 ml of 0,5 mol/l hydrochloric acid (4-2).

After adding 3 g of sodium chloride (4-7), bring to boiling to drive off the carbon dioxide. Allow to cool. Place the beaker on the magnetic stirrer (5-2) and insert the precalibrated pH meter electrodes (5-1).

Adjust the pH to exactly 6,3, first with the 0,5 mol/l sodium hydroxide solution (4-3), then with the 0,025 mol/l solution (4-4).

Add 20 g of D-mannitol (4-6), dissolve completely and mix thoroughly. Titrate with the 0,025 mol/l sodium hydroxide solution (4-4) to pH 6,3 (at least 1 minute stability). Let X1 be the volume required.

8-   Blank solution

Prepare a blank solution by repeating the whole procedure from the preparation of solution stage, omitting only the fertiliser. Let X_0 be the volume required.

9-   Boron (B) value of the sodium hydroxide solution (4-4)

Pipette 20 ml (2,0 mg B) of the calibration solution (4-5), into a 400 ml beaker and add several drops of methyl red indicator solution (4-1). Add 3 g of sodium chloride (4-7) and the hydrochloric acid solution (4-2) up to the point of change of the indicator solution (4-1).

Make up the volume to about 150 ml and bring gradually to the boil so as to eliminate carbon dioxide. Allow to cool. Place the beaker on the magnetic stirrer (5-2), and insert the precalibrated pH meter electrodes (5-1). Adjust the pH to exactly 6,3, first with the 0,5 mol/l sodium hydroxide solution (4-3), then with the 0,025 mol/l solution (4-4).

Add 20 g of D-mannitol (4-6), dissolve completely and mix thoroughly. Titrate with the 0,025 mol/l sodium hydroxide solution (4-4) to pH 6,3 (at least 1 minute stability). Let V_1 be the volume required.

Prepare a blank solution in the same way, substituting 20 ml of water for the calibration solution. Let V_0 be the volume required.

The boron value (F) in mg/ml of the standard NaOH solution (4-4) is as follows:

$$F(\text{in mg/l}) = 2/(V1 - V0)$$

1 ml of exactly 0,025 mol/l sodium hydroxide solution corresponds to 0,27025 mg B.

10-   Expression of results

The percentage of boron in the fertiliser is given by:

$$B(\%) = \frac{(X1 - X0) \times F \times V}{10 \times a \times M}$$

where

B (%) is the percentage of boron in the fertiliser;

X_1 is the volume, in ml, of the 0,025 mol/l sodium hydroxide solution (4-4); needed for the test solution;

X_0 is the volume, in ml, of the 0,025 mol/l sodium hydroxide solution (4-4); needed for the blank solution;

F is the boron (B) value, in mg/ml, of the 0,025 mol/l sodium hydroxide solution mol/l (4-4);

V is the volume, in ml, of the extract solution obtained in accordance with Method 10.1 or 10.2;

a is the volume, in ml, of the aliquot (7-1) taken from the extract solution (6-1);

M is the mass, in grams, of the test sample taken in accordance with Method 10.1 or 10.2.

Method 10.6
Determination of cobalt in fertiliser extracts by the gravimetric method with 1-nitroso-2-naphthol
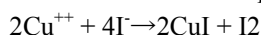
1-   Scope

This document defines a procedure for determining cobalt in fertilizer extracts.
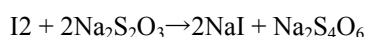
2-   Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Method 10.1 or Method 10.2 for which a declaration of cobalt content is required by Annex I E to this Regulation.

3-   Principle

Cobalt III combines with 1-nitroso-2-naphthol to give a red precipitate $Co(C_{10}H_6ONO)_3$, $2H_2O$. After the cobalt present in the extract has been brought to the cobalt III state, the cobalt is precipitated in an acetic acid medium by a solution of 1-nitroso-2-naphthol. After filtration, the precipitate is washed and dried to constant mass and then weighed as $Co(C_{10}H_6ONO)_3$, $2H_2O$.

4-   Reagents

4-1   Hydrogen peroxide solution (H_2O_2, d_{20} = 1,11 g/ml) 30 %

4-2   Sodium hydroxide solution, about 2 mol/l

Dissolve 8 g of sodium hydroxide in pellet form in 100 ml of water.

4-3   Diluted hydrochloric acid solution, about 6 mol/l

Mix one volume of hydrochloric acid (d_{20} = 1,18 g/ml) with 1 volume of water.

4-4   Acetic acid (99,7 % CH_3CO_2H) (d_{20} = 1,05 g/ml)

4-5   Acetic acid solution (1:2), about 6 mol/l

Mix one volume of acetic acid (4.4) with 2 volumes of water.

4-6   Solution of 1-nitroso-2-naphthol in 100 ml of acetic acid (4.4). Add 100 ml of lukewarm water. Mix thoroughly. Filter at once. The solution obtained must be used immediately

5-   Apparatus

5-1   Filter crucible P 16/ISO 4 793, porosity 4, capacity 30 or 50 ml

5-2   Drying oven at 130 (± 2) °C

6-   Preparation of the solution to be analysed

6-1   Preparation of the cobalt solution

See Methods 10.1 or 10.2.

6-2   Preparation of the solution to be analysed

Place an aliquot of the extract containing not more than 20 mg Co in a 400 ml beaker. If the extract is obtained according to Method 10.2, acidify with five drops of hydrochloric acid (4-3). Add about 10 ml of the hydrogen peroxide solution (4-1). Allow the oxidant to act in the cold state for 15 minutes, then make up to about 100 ml with water. Cover the beaker with a watch glass. Bring the solution to boiling point and allow to boil for about 10 minutes. Cool. Make alkaline with the sodium hydroxide solution (4-2) drop by drop until black cobalt hydroxide begins to precipitate.

7- Procedure

Add 10 ml of acetic acid (4-4) and make up the solution with water to about 200 ml. Heat until boiling. Using a burette, add 20 ml of the 1- nitroso-2-naphthol solution (4-6) drop by drop, stirring constantly. Complete by vigorous stirring to make the precipitate coagulate.

Filter through a previously weighed filter crucible (5-1), taking care not to clog up the crucible. With this in mind, ensure that liquid is left above the precipitate throughout the filtration process.

Wash the beaker with dilute acetic acid (4-5) to remove all the precipitate, wash the precipitate on the filter with dilute acetic acid (4-5) and then three times with hot water.

Dry in a drying oven (5-2) at 130 (± 2) °C until constant mass is achieved.

8- Expression of the results

1 mg of Co $(C_{10}H_6ONO)_3$, $2H_2O$ precipitate corresponds to 0,096381 mg Co.

The percentage of Cobalt (Co) in the fertiliser is given by:

$$Co(\%) = X \times 0.0096381 \times \frac{V \times D}{a \times M}$$

where

X is the mass in mg of the precipitate;

V is the volume in ml of the extract solution obtained in accordance with Method 10.1 or Method 10.2;

a is the volume in ml of the aliquot taken from the last dilution;

D is the dilution factor of this aliquot;

M is the mass in g of the test sample.

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Method 10.7

Determination of copper in fertiliser extracts by the titrimetric method

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1- Scope

This document defines a procedure for determining copper in fertilizer extracts.

2- Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Method 10.1 or Method 10.2 for which a declaration of copper content is required by Annex IE to this Regulation.

3- Principle

The cupric ions are reduced in an acidic medium with potassium iodide:

$$2Cu^{++} + 4I^- \rightarrow 2CuI + I2$$

The iodine released in this way is titrated with a standard sodium thiosulphate solution in the presence of starch as an indicator in accordance with:

$$I2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

4- Reagents

4-1 Nitric acid (HNO_3, d_{20} = 1,40 g/ml)

4-2 Urea $[(NH_2)_2 C = 0]$

4-3 Ammonium bifluoride (NH_4HF_2) solution 10 % w/v
Keep the solution in a plastic container.

4-4 Ammonium hydroxide solution (1 + 1)
Mix 1 volume of ammonia (NH_4OH, d_{20} = 0,9 g/ml) with 1 volume of water.

4-5 Sodium thiosulphate standard solution
Dissolve 7,812 g of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) with water in a 1 litre volumetric flask. This solution must be prepared so that 1 ml = 2 mg Cu. For stabilisation, add several drops of chloroform. The solution must be kept in a glass container and protected from direct light.

4-6 Potassium iodide (KI)

4-7 Potassium thiocyanate (KSCN) solution (25 % w/v)
Keep this solution in a plastic flask.

4-8   Starch solution (about 0,5 %)

Place 2,5 g of starch in a 600 ml beaker. Add about 500 ml of water. Boil while stirring. Cool to ambient temperature. The solution has a short preservation period. Its preservation can be extended by adding about 10 mg of mercury iodide.

5- Preparation of the solution to be analysed

Preparation of the copper solution

See Methods 10.1 and 10.2.

6- Procedure

6-1   Preparation of the solution of titration

Place an aliquot portion of the solution containing not less than 20-40 mg Cu in a 500 ml Erlenmeyer flask.

Drive off any excess oxygen present by boiling briefly. Make up to a volume of about 100 ml water. Add 5 ml of nitric acid (4-1), bring to boiling and allow to boil for about half a minute.

Remove the Erlenmeyer flask from the heating apparatus, add about 3 g of urea (4-2) and resume boiling for about half a minute.

Remove from the heating apparatus and add 200 ml of cold water. Where necessary, cool the contents of the Erlenmeyer flask to ambient temperature.

Gradually add ammonia hydroxide solution (4-4) until the solution becomes blue, then add 1 ml in excess.

Add 50 ml of ammonium bifluoride solution (4-3) and mix.

Add 10 g of potassium iodide (4-6) and dissolve.

6-2   Titration of the solution

Place the Erlenmeyer flask on a magnetic stirrer. Insert the rod into the Erlenmeyer flask and adjust the stirrer to the desired speed.

Using a burette, add standard sodium thiosulphate solution (4-5) until the brown colour of the iodine released from the solution becomes less intense.

Add 10 ml of the starch solution (4-8).

Continue to titrate with the sodium thiosulphate solution (4-5) until the purple colour has almost disappeared.

Add 20 ml of the potassium thiocyanate solution (4-7) and continue titration until the violet blue colour has completely disappeared.

Note the volume for thiosulphate solution employed.

7- Expression of results

1 ml of standard sodium thiosulphate solution (4-5) corresponds to 2 mg Cu.

The percentage of copper in the fertiliser is given by:

$$Cu(\%) = X \frac{V}{a \times M \times 5}$$

where

X is the volume in ml of the sodium thiosulphate solution used;

V is the volume in ml of the extract solution in accordance with Methods 10.1 and 10.2;

a is the volume in ml of the aliquot portion;

M is the mass in g of the test sample treated in accordance with Methods 10.1 and 10.2.

Method 10.8

Determination of iron in fertiliser extracts by atomic absorption spectrometry

1- Scope

This Method describes a procedure for determining iron in fertilizer extracts.

2- Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of total and/or water-soluble iron is required by Annex I E to this Regulation.

3- Principle

After suitable treatment and dilution of the extract, the iron content is determined by atomic absorption spectrometry.

4- Reagents

4-1 Hydrochloric acid solution, about 6 mol/l
See Method 10.4 (4-1).

4-2 Hydrochloric acid solution, about 0,5 mol/l
See Method 10.4 (4-2).

4-3 Hydrogen peroxide solution (30 % H_2O_2, d_{20} = 1,11 g/ml) free from micro-nutrients

4-4 Lanthanum salt solutions (10 g of La per litre)
See Method 10.4 (4-3).

4-5 Iron calibration solution

4-5-1 Iron stock solution (1 000 μg/ml)
In a 500 ml beaker, weigh to the nearest 0,1 mg, 1 g of pure iron wire, add 200 ml of 6 mol/l hydrochloric acid (4-1) and 15 ml of hydrogen peroxide solution (4-3). Heat on a hotplate until the iron is completely dissolved. When cool, transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume with water and mix thoroughly.

4-5-2 Iron working solution (100 μg/ml)
Place 20 ml of the stock solution (4-5-1) in a 200 ml volumetric flask. Make up to volume with the 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

5- Apparatus

Atomic absorption spectrometer: see Method 10.4 (5). The instrument must be fitted with a source of emitted radiation characteristic of iron (248,3 nm).

6- Preparation of the solution to be analysed

6-1 Iron extract solution
See Methods 10.1 and/or 10.2 and, if appropriate, 10.3.

6-2 Preparation of the test solution
See Method 10.4 (6-2). The test solution must contain 10 % (v/v) of a lanthanum salt solution.

7- Procedure

7-1 Preparation of blank solution
See Method 10.4 (7-1). The blank solution must contain 10 % (v/v) of the lanthanum salt solution used in 6-2.

7-2 Preparation of calibration solutions
See Method 10.4 (7-2).
For an optimum determination range of 0 to 10 μg/ml of iron, place 0,b 2, 4, 6, 8 and 10 ml respectively of working solution (4-5-2) in a series of 100 ml volumetric flasks. If necessary adjust the hydrochloric acid concentration as closely as possible to that of the test solution. Add 10 ml of the lanthanum salt solution used in 6-2. Make up to volume with 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly. These solutions contain 0, 2, 4, 6, 8 and 10 μg/ml respectively of iron.

7-3 Determination
See Method 10.4 (7.3). Prepare the spectrometer (5) for measurement at a wavelength of 248,3 nm.

8- Expression of results

See Method 10.4 (8).
The percentage of iron in the fertiliser is given by:
$$Fe\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$
If Method 10.3 is used:
$$Fe\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$
Where

Fe is the quantity of iron expressed as a percentage of the fertiliser;

x_s is the concentration in μg/ml of the test solution (6-2);

x_b is the concentration in μg/ml of the blank solution (7-1);

V is the volume in ml of extract obtained in accordance with Method 10.1 or 10.2;

D is the factor of dilution carried out in 6-2;

M is the mass in grams of the test sample taken in accordance with Method 10.1 or 10.2.

Calculation of the dilution factor D: if (a_1), (a_2), (a_3), ···, (ai) and (a) are aliquot portions and (v_1), (v_2), (v_3), ···, (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D is given by:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times. \times (Vi/ai) \times (100/a)$$

Method 10.9
Determination of manganese in fertiliser extracts by titration

1- Scope

This Method describes a procedure for determining manganese in fertiliser extracts.

2- Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of manganese is required by Annex I E to this.

3- Principle

If chloride ions are present in the extract, they are driven off by boiling the extract with sulphuric acid. The manganese is oxidized by sodium bismuthate in a nitric acid medium. The permanganate formed is reduced by an excess of ferrous sulphate. This excess is titrated with a potassium permanganate solution.

4- Reagents

4-1 Concentrated sulphuric acid (H_2SO_4, d_{20} = 1,84 g/ml)

4-2 Sulphuric acid, about 9 mol/l

Carefully mix 1 volume of concentrated sulphuric acid (4-1) with 1 volume of water.

4-3 Nitric acid, 6 mol/l

Mix 3 volumes of nitric acid (HNO_3, d_{20} = 1,40 g/ml) with 4 volumes of water.

4-4 Nitric acid, 0,3 mol/l

Mix 1 volume of 6 mol/l nitric acid with 19 volumes of water.

4-5 Sodium bismuthate ($NaBiO_3$) (85 %).

4-6 Kieselguhr

4-7 Orthophosphoric acid, 15 mol/l (H_3PO_4, d_{20} = 1,71 g/ml)

4-8 Ferrous sulphate solution, 0,15 mol/l

Dissolve 41,6 g of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) in a 1 litre volumetric flask.

Add 25 ml of concentrated sulphuric acid (4.1) and 25 ml phosphoric acid (4-7). Make up to 1 000 ml. Mix.

4-9 Potassium permanganate solution, 0,020 mol/l

Weigh out 3,160 g of potassium permanganate ($KMnO_4$) to within 0,1 mg. Dissolve and make up to 1 000 ml with water.

4-10 Silver nitrate solution, 0,1 mol/l

Dissolve 1,7 g of silver nitrate ($AgNO_3$) in water and make up to 100 ml.

5- Apparatus

5-1 Filter crucible P16/ISO 4 793, porosity 4, capacity 50 ml, mounted on a 500 ml filtration flask.

5-2 Magnetic stirrer

6- Preparation of the solution to be analysed

6-1 Manganese extract solution

See Methods 10.1 and 10.2. If it is not known whether chloride ions are present, perform a test on the solution with one drop of the silver nitrate solution (4-10).

6-2 In the absence of chloride ions, place an aliquot of the extract containing 10 to 20 mg of manganese in a tall form 400 ml beaker. Bring to a volume of about 25 ml either by evaporation or by adding water. Add 2 ml of concentrated sulphuric acid (4-1)

6-3 If chloride ions are present, it is necessary to remove them as follows

Place an aliquot of the extract containing 10 to 20 mg of manganese in a tall form 400 ml beaker. Add 5 ml of 9 mol/l sulphuric acid (4-2). Under a fume hood, bring to boiling on a hotplate and allow to boil until copious white fumes are released. Continue until the volume is reduced to about 2 ml (thin film of syrupy liquid at the bottom of the beaker). Allow to cool to ambient temperature.

Carefully add 25 ml of water and once again test for the presence of chlorides with one drop of the silver nitrate solution (4-10). If chlorides still remain, repeat the operation after adding 5 ml of 9 mol/l sulphuric acid (4-2).

7- Procedure

Add 25 ml of 6 mol/l nitric acid (4-3) and 2,5 g of sodium bismuthate (4-5) to the 400 ml beaker containing the test solution. Stir vigorously for three minutes on the magnetic stirrer (5-2).

Add 50 ml of 0,3 mol/l nitric acid (4-4) and stir again. Filter in vacuo through a crucible (5-1), the bottom of which is covered with Kieselguhr (4-6). Wash the crucible several times with the 0,3 mol/l nitric acid (4-4) until a colourless filtrate is obtained.

Transfer the filtrate and the washing solution into a 500 ml beaker. Mix and add 25 ml of 0,15 mol/l ferrous sulphate solution (4-8). If the filtrate turns yellow after the addition of ferrous sulphate, add 3 ml of 15 mol/l orthophosphoric acid (4-7).

Using a burette, titrate the excess ferrous sulphate with 0,02 mol/l potassium permanganate solution (4-9) until the mixture turns pink, the colour remaining stable for one minute. Perform a blank test under the same conditions, omitting only the test sample.

N o t e

The oxidised solution must not come into contact with rubber.

8- Expression of results

1 ml of 0,02 mol/l potassium permanganate solution corresponds to 1,099 mg of manganese (Mn).

The percentage of manganese in the fertiliser is given by:

$$Mn(\%) \text{where} = (Xb - Xs) \times 0.1099 \times \frac{V}{a \times M}$$

Where

x_b is the volume in ml of the permanganate used for the blank;

x_s is the volume in ml of the permanganate used for the test sample;

V is the volume in ml of the extract solution in accordance with Methods 10.1 and 10.2;

a is the volume in ml of the aliquot portion taken from the extract;

M is the mass in g of the test sample.

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Method 10.10

**Determination of molybdenum in fertiliser extracts by the gravimetric
method with 8-Hydroxyquinoline**

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1- Scope

This document describes a procedure for determining molybdenum in fertiliser extracts.

2- Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of molybdenum is required by Annex I E to this Regulation.

3- Principle

The molybdenum level is determined by precipitation as molybdenyl oxinate under specific conditions.

4- Reagents

4-1 Sulphuric acid solution, approximately 1 mol/l

Carefully pour 55 ml of sulphuric acid (H_2SO_4, d_{20} = 1,84 g/ml) into a 1 litre volumetric flask containing 800 ml of water. Mix. After cooling, make up to one litre. Mix.

4-2   Diluted ammonia solution (1: 3)

Mix 1 volume of concentrated ammonia solution (NH_4OH, d_{20} = 0,9 g/ml) with 3 volumes of water.

4-3   Diluted acetic acid solution (1: 3)

Mix 1 volume of concentrated acetic acid (99,7 % CH_3COOH, d_{20} = 1,049 g/ml) with 3 volumes of water.

4-4   Solution of disodium salt of ethylene diamine tetraacetic acid (EDTA)

Dissolve 5 g of Na_2EDTA in water in a 100 ml volumetric flask. Make up to the calibration mark and mix.

4-5   Buffer solution

In a 100 ml volumetric flask, dissolve 15 ml of concentrated acetic acid and 30 g of ammonium acetate in water. Make up to 100 ml.

4-6   7-Hydroxyquinoline (oxine) solution

In a 100 ml volumetric flask, dissolve 3 g of 8-Hydroxyquinoline in 5 ml of concentrated acetic acid. Add 80 ml of water. Add the ammonia solution (4-2) drop by drop until the solution becomes cloudy and then add the acetic acid (4-3) until the solution becomes clear again.

Make up to 100 ml with water.

5-   **Apparatus**

5-1   Filter crucible P16/ISO 4 793, porosity 4, capacity 30 ml

5-2   pH meter with glass electrode

5-3   Drying oven at 130 to 135 °C

6-   **Preparation of the solution to be analysed**

6-1   Preparation of the molybdenum solution. See Method 10.1 and Method 10.2

7-   **Procedure**

7-1   Preparation of the test solution

Place an aliquot portion containing 25 to 100 mg Mo in a 250 ml beaker. Make up the volume to 50 ml with water.

Adjust this solution to pH of 5 by adding the sulfuric acid solution (4-1) drop by drop. Add 15 ml of EDTA solution (4-4) and then 5 ml of buffer solution (4-5). Make up to about 80 ml with water.

7-2   Obtaining and washing the precipitate

Obtaining the precipitate

Heat the solution slightly. Stirring constantly, add the oxine solution (4-6). Continue the precipitation until formation of a deposit is no longer observed. Add further reagent until the supernatant solution turns slightly yellow. A quantity of 20 ml should normally be sufficient. Continue to heat the precipitate slightly for two or three minutes.

Filtration and washing

Filter through a filter crucible (5-1). Rinse several times with 20 ml of hot water. The rinse water should gradually become colourless indicating that oxine is not longer present.

7-3   Weighing the precipitate

Dry the precipitate at 130 to 135 °C to constant mass (at least one hour).

Allow to cool in a desiccator and then weigh.

8-   **Expression of the results**

1 mg of molybdenyl oxinate, $MoO_2(C_9H_6ON)_2$, corresponds to 0,2305 mg Mo.

The percentage of molybdenum in the fertiliser is given by:

$$Mo(\%) = X \times 0.02305 \times \frac{V \times D}{a \times M}$$

Where

X is the mass in mg of the molybdenyl oxinate precipitate;

V is the volume in ml of the extract solution in accordance with Methods 10.1 or 10.2;

a is the volume in ml of the aliquot taken from the last dilution;

D is the dilution factor of the aliquot;

M is the mass in g of the test sample.

Method 10.11

Determination of zinc in fertiliser extracts by atomic absorption spectrometry

1-   Scope

This Method describes a procedure for determining zinc in fertilizer extracts.

2-   Field of application

This procedure is applicable to extracts from samples of fertilizers obtained by Methods 10.1 and 10.2 for which a declaration of zinc is required by Annex I E to this Regulation.

3-   Principle

After suitable treatment and dilution of the extracts, the zinc level is determined by atomic absorption spectrometry.

4-   Reagents

4-1   Hydrochloric acid solution, about 6 mol/l

See Method 10.4 (4-1).

4-2   Hydrochloric acid solution, about 0,5 mol/l

See Method 10.4 (4-2).

4-3   Lanthanum salt solutions (10 g of La per litre)

See Method 10.4 (4-3).

4-4   Zinc calibration solutions

4-4-1   Zinc stock solution (1 000 μg/ml)

In a 1 000 ml volumetric flask, dissolve 1 g of zinc powder or flakes weighed to within 0,1 mg in 25 ml of 6 mol/l hydrochloric acid (4-1). When completely dissolved, make up to volume with water and mix thoroughly.

4-4-2   Zinc working solution (100 μg/ml)

In a 200 ml volumetric flask, dilute 20 ml of the stock solution (4-4-1) in 0,5 mol/l hydrochloric acid solution (4-2). Make up to a volume with the 0,5 mol/l hydrochloric acid solution and mix thoroughly.

5-   Apparatus

Atomic absorption spectrometer.

See Method 10.4 (5). The apparatus must be fitted with a source of lines characteristic of zinc (213,8 nm). The spectrometer must allow background correction to be made.

6-   Preparation of the solution to be analysed

6-1   Zinc extract solution

See Method 10.1 and/or 10.2.

6-2   Preparation of the test solution

See Method 10.4 (6.2). The test solution must contain 10 % by volume of lanthanum salt solution (4.3).

7-   Procedure

7-1   Preparation of the blank solution

See Method 10.4 (7-1). The blank solution must contain 10 % by volume of the lanthanum salt solution used in 6-2.

7-2   Preparation of the calibration solutions

See Method 10.4 (7-2). For an optimum interval of 0 to 5 μg/ml of zinc, place 0, 0,5, 1, 2, 3, 4 and 5 ml, respectively, of the working solution (4-4-2) in a series of 100 ml

volumetric flasks. Where necessary, adjust the concentration of hydrochloric acid to bring it as close as possible to that of the test solution. Add 10 ml of the lanthanum salt solution used in (6-2) to each volumetric flask. Make up to 100 ml with the 0,5 mol/l hydrochloric acid solution (4-2) and mix thoroughly.

These solutions contain, respectively, 0, 0,5, 1, 2, 3, 4 and 5 μg/ml of zinc.

7-3   Determination

See Method 10.4 (7-3). Prepare the spectrometer (5) for measurements at a wavelength of 213,8 nm.

8-   Expression of results

See Method 10.4 (8).

The percentage of zinc in the fertiliser is given by:

$$Zn\% = ((Xs - Xb) \times V \times D)/(M \times 10^4)$$

If Method 10.3 has been used:

$$Zn\% = ((Xs - Xb) \times V \times 2D)/(M \times 10^4)$$

Where

Zn is the quantity of zinc expressed as a percentage of the fertiliser;

x_s is the concentration in μg/ml of the test solution;

x_b is the concentration in μg/ml of the blank solution;

V is the volume in ml of the extract solution obtained in accordance with Method 10.1 or 10.2;

D is the factor corresponding to the dilution performed in (6.2);

M is the mass in g of the test sample taken in accordance with Method 10.1 or 10.2.

Calculation of the dilution factor D:

where (a_1), (a_2), (a_3), ⋯, (ai) and (a) are successive aliquot portions and (v_1), (v_2), (v_3), ⋯, (vi) and (100) are the volumes in ml corresponding to their respective dilutions, the dilution factor D is given by:

$$D = (V1/a1) \times (V2/a2) \times (V3/a3) \times … \times (Vi/ai) \times (100/a)$$

Methods 11
Chelating agents

Method 11.1
Determination of the chelated micro-nutrient content and of the chelated
fraction of micro-nutrients

EN 13366: Fertilisers — Treatment with a cation exchange resin for the determination of the chelated micro-nutrient content and of the chelated fraction of micro-nutrients
This method of analysis has been ring-tested.

Method 11.2
Determination of EDTA, HEDTA and DTPA

EN 13368-1: Fertilisers — Determination of chelating agents in fertilisers by ion chromatography — Part 1: EDTA, HEDTA and DTPA
This method of analysis has been ring-tested.

Method 11.3
Determination of iron chelated by o,o EDDHA and o,o EDDHMA and HBED

EN 13368-2: Fertilizers – Determination of chelating agents in fertilizers by chromatography. Part 2: Determination of Fe chelated by o,o-EDDHA, o,o-EDDHMA and HBED by ion pair-chromatography
This method of analysis has been ring-tested.

Method 11.4
Determination of iron chelated by EDDHSA

EN 15451: Fertilisers — Determination of chelating agents-Determination of iron chelated by EDDHSA by ion pair-chromatography
This method of analysis has been ring-tested.

Method 11.5
Determination of iron chelated by o,p EDDHA
EN 15452: Fertilisers — Determination of chelating agents-Determination of iron chelated by o,p EDDHA by reversed phase HPLC
This method of analysis has been ring-tested.

Method 11.6
Determination of IDHA
EN 15950: Fertilizers – Determination of N-(1,2-dicarboxyethyl)-D,L-aspartic acid (Iminodisuccinic acid, IDHA) using high- performance liquid chromatography (HPLC)
This method of analysis has been ring-tested.

Method 11.7
Determination of lignosulfonates
EN 16109: Fertilizers – Determination of micro-nutrient ions complexed in fertilizers – Identification of lignosulfonates
This method of analysis has been ring-tested.

Method 11.8
Determination of the complexed micro-nutrient content and of the complexed fraction of micro-nutrients
EN 15962: Fertilizers – Determination of the complexed micro-nutrient content and of the complexed fraction of micro- nutrients
This method of analysis has been ring-tested.

Methods 12
Nitrification and urease inhibitors

Method 12.1
Determination of dicyandiamide
EN 15360: Fertilisers — Determination of dicyandiamide – Method using highperformance liquid chromatography (HPLC)
This method of analysis has been ring-tested.

Method 12.2
Determination of NBPT
EN 15688: Fertilisers — Determination of urease inhibitor N-(n-butyl)thiophosphoric triamide (NBPT) using high-performance liquid chromatography (HPLC)
This method of analysis has been ring-tested.

Method 12.3
Determination of 3-methylpyrazole
EN 15905: Fertilizers – Determination of 3-methylpyrazole (MP) using high-performance liquid chromatography (HPLC)
This method of analysis has been ring-tested.

Method 12.4
Determination of TZ

EN 16024: Fertilizers – Determination of 1H,1,2,4-triazole in urea and in fertilizers containing urea – Method using high- performance liquid chromatography (HPLC)
This method of analysis has been ring-tested.

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Method 12.5
Determination of 2-NPT
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EN 16075: Fertilizers – Determination of N-(2-nitrophenyl)phosphoric triamide (2-NPT) in urea and fertilizers containing urea – Method using high-performance liquid chromatography (HPLC)
This method of analysis has been ring-tested.

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Methods 13
Heavy metals

Method 13.1
Determination of cadmium content
</div>

EN 14888: Fertilisers and liming materials — Determination of cadmium content
This method of analysis has been ring-tested.

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