THIN-LAYER CHROMATOGRAPHY FOR DEMONSTRATING CHLORIDE ION AND ITS CATIONS IN CONCRETE SAMPLES

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Abstract

The mobility, the ability for reactions and boundability of chloride ions depend on the type of cations that is present in the concrete. This is why it is important to detect the cations and their mobility.

In our experiments we have tried to detect chloride ions bounded to different (Ca^{++}, Mg^{++}, Na^+ and K^+) ions by thin-layer chromatography.

As thin layer we used silica gel, aluminium oxide, MN cellulose. As eluent we used acetone-butanol-ccNH$_4$OH-water(65:20:10:5 v/v) composition.

We made visible the chlorides by the solution of $AgNO_3$ and different indicators, like bromocresol purple, fluorescein, alcoholic solution of dichlorofluorescein (DCF) and the mixture of bromocresol green and methyl red.

To detect the Ca^{++}, Mg^{++}, Na^+, and K^+ ions we used different reagents.

Significant colour-reactions were produced by cations in a larger quantity than 5 μg.

The process seems to be good to detect qualitatively the chlorides and the chloride ions bounded to cations.

Keywords: thin-layer chromatography, chloride ion, cations in concrete.

Introduction

There are several methods for determining chloride content in concrete. Most of them rely on the principle of chloride detection by argentometry. These methods are indifferent to the kind of cation bounded to the chloride.

Part of chlorides in the concrete are bounded by tricalcium-aluminates in form of Friedel salt, that is, however, sensitive to the medium pH, and decomposes even in the mildly basic pH domain (7.5 to 9.5), to release chloride ions. Disengaged free chloride ions cause reinforcement corrosion.

Chloride mobility is affected by the kind of adjacent cations, affecting migration of chloride ions in the pore structure of reinforced concrete. The effect of cations is of importance also from other aspects. Alkali ions are known since long to impair concrete stability. This is why Na$_2$O and K$_2$O contents of cement are limited in standard specifications. Alkali ions attack

feldspar in aggregates to produce swelling products of corrosion, disrupting the concrete structure.

In addition to the main mass of calcium ions in the concrete, detection of chlorides bounded to alkali and magnesium ions is of high importance, informing of their mobility, and of the concrete structure stability.

Thin-layer chromatography makes use of exactly different ion mobilities to demonstrate the presence of cations bounded to chloride.

Water-soluble chlorides may enter concrete either as accelerators or via salting in winter [1]. De-icer salting is made mostly with NaCl, sometimes with $MgCl_2$ or carbamide.

Chlorides applied as accelerators are either of neutral (KC1) or of mildly acid ($CaCl_2$, $MgCl_2$) reaction. Carbonates and hydroxides applied for de-icing beside chlorides are of basic reaction. Several admixtures intermingle chlorides, carbonates and hydroxides. Chloridic agents are actually being avoided.

Slight quantities of admixtures do not affect significantly the highly basic pH of the aqueous suspension of concrete grind [10-11], but any anion soluble in water, in particular carbonate and hydroxide, disturb $AgNO_3$ detection of chloride ion.

There are hardly data in the special literature for separation and detection of chlorides, even textbooks on layer chromatography [2,3].

Separation of halogenide ions was made on silica gel [3], aluminium oxide [5] and MN cellulose 300 layers [6]. In case of silica gel layer, one component of the eluent was benzyl-amine. Before utilization, the aluminium oxide layer was treated with nitric acid solution, applying 0.2 m KNO_3 solution as eluent. Water and aqueous solutions ra'se in the layer rather slowly. In these cases the running time is 60 to 120 min. The application of the cellulose layer seemed the most convenient.

Polar solvents or solvent systems suit running of chlorides. Because of the solubility of anorganic salts, in general, eluent has to contain water.

A special reaction of detecting chloride ion is AgCl precipitation. This reaction is rather sensitive in aqueous solutions, $KH = 5~\mu g - Cl^-$. In fact the other reagents proposed in literature act as acid base indicators on the sorbent. Such indicators are e.g. fluorescein [7], bromocresol purple [7], dichlorofluorescein [8].

Previous results connected with separation of chloride ion and its cations on thin-layer chromatography have been shown in this paper.

Experimental Part

Preparation of samples:

  2 g of concrete grind are suspensed in 10 ml of distilled water, shaken for 30 min, or soaking for a night, then filtrated on blue striped filter paper. 10 μl of the solution are dripped on the layer. For an ordinary concrete, 1 μl of the solution contains 0.1 μg of chloride.

Standard solutions:

$CaCl_2$	0.5μ g/μl	solution
NH_4Cl	0.6μ g/μl	solution
NH_4Cl	2.0μ g/μl	solution

  Thin layer: Factory-made layer, 0.1 mm thick, named 'Cellulose $F_2 54$' (Merck, Art. 5574)

Eluent: Acetone – butanol – cc.NH_4OH – water (65:20:10:5 v/v)

Reagents for visualization:

$AgNO_3$ solution (0.5 and 1.0 %)

0.1 % bromocresol purple solution (alcoholic)

0.1 % fluorescein solution (alcoholic)

0.1 % dichlorofluorescein solution (alcoholic)

0.1 % mix indicator:

  3 parts of bromocresol green indicator

  1 part of methyl red solution

  Special reagents for detecting of Ca^{++}, Mg^{++}, Na^+ and K^+ions [9]:

In case of Ca^{++}

  1 8-hydroxychinoline for detection of Ca^{++}, Ba^{++} and Sr^{++} ions [10].

  2 Diphenyl carbazide for detection of Ca^{++}, Pb^{++}, Sn^{++}, etc. ions [11].

In case of Mg^{++}

  Quercetin for detecting Mg^{++}, Al^{+++}, uranyle and wolframate ions [12], [13].

In case of K^+

  1 Reaction of K^+ ions with Na-tetraphenyl borate-Rhodamine B [14].

  2 Detection of K^+ ions by means of cobalt-lead-nitrite [15].

In case of Na^+

  Detection of Na^+ ions with Zn-uranyle acetate [16].

Results

Detection of Chloride Ion:

On a cellulose layer run with an eluent of acetone-butanol-ccNH_4OH water (65:20:10:5 v/v) composition, with a bromocresol purple indicator, purple

spots on yellow background appeared in starting point, (respectively near of starting point). Under such circumstances NH_4Cl could not be detected. This means that discoloration does not belong to the chloride ions, but to the pertaining cations. In an eluent containing NH_4OH — depending on their bases — chlorides may run even on the layer as NH_4Cl. Bromocresol purple is an acid-basis indicator. Its range of conversion from yellow to purple is from pH 5.2 to 6.8. NH_4Cl reacts as acidic.

Under such conditions, after development, spraying with a mix indicator bluish green spots over pink background appeared, caused by cations.

With dichlorofluorescein indicator the cations appear as orange spots on yellow background in the starting point, but in addition, spots lighter than the background appear on the layer, with 0.25 R_f value. The light spot appears also for NH_4Cl, hence this is the spot of the chloride ion.

Spraying the layer developed with dichlorofluorescein (DCF) also with an $AgNO_3$ solution, spots better distinatible on the brownish background than the light ones appear, in particular, if 0.5 % rather than 1.0 % $AgNO_3$ solution is applied.

Using a DCF + $AgNO_3$ solution, presence of chloride ions may be proven also in the concrete samples, doubtless higher than 0.05 %, namely an ordinary concrete sample (with 0.05 % of chloride) did not exhibit any discoloration under the same conditions.

In fact, for detection of chloride ions the cellulose layer has been found to be the most convenient one. Acetone butanol ccNH_4OH water (65:20:10:5 v/v) may be applied as eluent. Combined use of DCF + $AgNO_3$ solution proved to be the best for visualization. In UV light the spots are darkened. In this system the chloride ion runs with 0.25 R_f value, the cations remain near the starting point.

Detection of Cations at Chloride Ion from the Watery Extract of Concrete Grind

Our experiments aimed at developing a method suiting to identity Ca^{++}, Mg^{++}, Na^+ and K^+ ions. Applied stock solutions were:

1. Standard solutions:

			Cl^- $\mu g/\mu l$	cation $\mu g/\mu l$
40.0 mg	$CaCl_2$ $2H_2O$/ 10 ml	water	1.93	1.09
53.2 mg	NaCl / 10 ml	water	3.23	2.09
59.6 mg	KCl / 10 ml	water	2.83	3.12
109.0 mg	$MgCl_2 6H_2O$ /10 ml	water	3.80	1.30

(Sample 'Ö' =the four standards together)

2. Sample 'E' = referens concrete extract
3. " 'I' = concrete extract with known chloride content
   " (extract of concrete sample with 0.25% NaCl).
4. " 'A' = extract with unknown chloride content

From the standard solutions, 2, 3 and 5 μl, from samples 'E', 'I' and 'A' 10 or 15 μl have been dropped on the cellulose layer. Running was made in an eluent composed of acetone-water (4:1:1 v/v) in the first stage of the tests. Subsequently, running was made in a mix of alcohols containing NH_4OH.

Our test showed that none of the special reagents above produced a significant colour reaction in the presence of 5 μg or less of Ca^{++}, Mg^{++}, Na^+ or K^+. A spot visible to the naked eye was only observed for a cobalt-lead-nitrite sprayed, in the case of K^+ (9.7 μg). Though, in spraying by means of solution DCF + $AgNO_3$, sharp outlined spots appeared.

R_f values of spots pertaining to the standard samples on a cellulose layer, for an acetone-water (4:1 v/v) eluent:

Table 1
R_f values of the standard samples

sample	R_f value
NaCl	0.25
KCl	0.20
$MgCl_2$	0.14
$CaCl_2$	0.12

After visualization by DCF + $AgNO_3$ solution we have got only one spot. It seems, that most part of chlorides runs as a non-dissociated molecule in the lowly polar eluent.

In the case above, various chloride solution were dropped on each 10 μl of extract 'E', to let standards run under the same circumstances as samples 'E' and sample 'E' permitted no detection of Cl^-, but for 'I' a marked chloride spot appeared, and its R_f value hinted to the presence of NaCl.

In an eluent containing ethyl-acetate (acetone-ethyl-acetate-water (4:1:1 v/v)), R_f values were lower, but the order was the same.

In the highly polar solvent system the chlorides of alkali and alkaline earth metals run in dissociated form, and the different cations and the chloride ion run with various R_f values on the cellulose layer.

In case of ethanol-methanol-ccNH_4OH (3:2:1 v/v), after visualization with DCF + $AgNO_3$ solution the R_f values are as follows:

Table 2

R_f values of the ions detected

ion	R_f value
Cl^-	0.40
Na^+	0.26
K^+	0.17
Ca^{++}	0.11
Mg^{++}	0.00

(In the case of $MgCl_2$ there is a diffuse strip under the spot of the Cl^-, between 0.00 and 0.40). By means of solvent system above, we obtained the best separation. In this case below the clearer chloride ion spot the darker, brownish spots of alkali and alkaline earth metal cations appear. So their indentification can be achieved.

Consequently, while in highly polar solvent system containing NH_4OH both the spot of chloride ion and spots of cations appear after visualization with DCF + $AgNO_3$ solution, in case of acetone-water (4:1 v/v) eluent the chlorides of alkali and alkaline earth metal are concentrated in one spot, hence the chloride ion does not separate (or only partially) from the related cation.

This is in accordance with the experience of other authors [6], who did not demonstrate two separated spots in case of NaCl in the 80 % (v/v) acetone-water eluent.

In our opinion the separation of the alkali and alkaline earth metal chlorides on cellulose layer depends, besides the solvent, upon the solubility and electronegativity of the salts, upon the ion-exchange etc. as well.

Conclusion

In the thin-layer chromatography determination on cellulose layer of chlorides in concrete, both alcohols containing NH_4OH and an acetone-water mixture may be applied as eluents. Most of information is obtained from the use of solutions of 0.1 % DCF + $AgNO_3$ for visualization. Spots may be darkened by UV radiation. Thus, the method of thin layer chromatography suits qualitative detection of chlorides and cations bound to chlorides. This method is actually at laboratory level, but it is expected to be developed into an in-situ method. Its application is advantageous since detection of the tested cations found to chlorides in such a low concentration would require a relatively intricate laboratory technique.

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