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Abstract

Separation and determination of some organic acids, mono-carboxylic (formic and acetic), dicarboxylic (oxalic and tartaric), tricarboxylic (citric) acids and aromatic acids (phtalic, benzoic, mellitic and trimellitic), by capillary electrophoresis are reviewed. The method development parameters, such as separation and injection mode, are discussed. Special attention is paid to the comparison of different detection types (spectroscopic and electrochemical). The optimisation of the carrier electrolyte composition (choice of carrier electrolyte, effect of pH, ionic strength, electro-osmotic flow modifier) is treated. Different additives (alkali-earth and transition metal ions, cyclodextrins and alcohol), which are often used for improving organic acid separation, are also considered.

Contents

1. Introduction

Uranium monocarbide (UC) or mixed carbide (U,Pu)C may find an application as fuel for nuclear reactors of IVth generation. If an aqueous reprocessing of the carbide fuel is to be considered, the dissolution process of the irradiated UC (or (U,Pu)C) becomes of great importance.

The electrochemical dissolution of carbide fuels in aqueous solutions leads to the formation of a number of organic species [1, 2] which could cause serious interferences in the subsequent steps of reprocessing, in particular, the emulsion formation in the solvent extraction steps and complexation with U(VI) and Pu(IV) resulting in an incomplete extraction of these ions [3]. The quantity of organic products which can be formed depends on the electrochemical parameters of dissolution, the nature and concentration of electrolyte *etc.* In order to achieve the optimal conditions of dissolution with formation of a minimum of dissolved organic species, a reliable method for the simultaneous determination of organic species is needed.

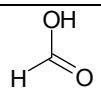
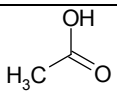
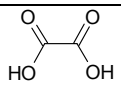
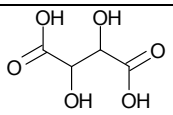
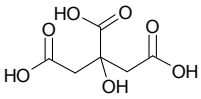
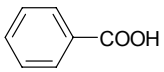
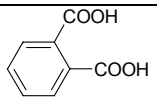
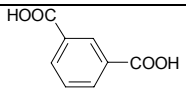
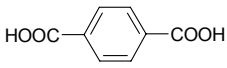
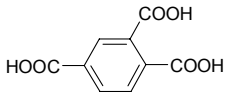
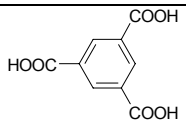
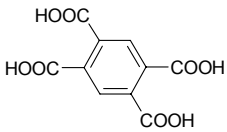
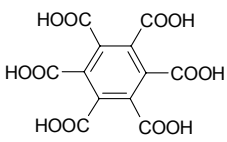
The identification of all soluble products which issue from the dissolution of carbides has not been completed. Only oxalic, mellitic and acetic have been identified [1, 2, 4]. In ref. [4], compounds of high molecular mass (about 200 g/M) were pointed out. Two groups of acids: aliphatic and aromatic, were found. In table 1, some data on a number of aliphatic and aromatic acids are given. Aliphatic acids are well miscible with water, contrary to aromatic acids which are only slightly miscible with water.

Within the last few years, capillary electrophoresis (CE) has been recognized as an attractive technique for the separation and quantification of organic and inorganic cations and anions. It is also widely used for the separation and

determination of short-chain carboxylic acid anions. In the determination of aromatic acid anions, CE is rarely applied. CE offers also some attractive features including short analysis time, high numbers of theoretical plates and separation selectivities completely different from chromatographic methods. CE has been shown to be a good alternative method to chromatography, requiring almost no sample preparation, other than dilution. The other advantages of CE include low reagent consumption, relatively low cost, small sample amount requirements, and aptitude for automation.

A lot of information about the separation of short chain organic acids by CE has been available in the literature (Tables 2-6) but the works on the separation and determination of aromatic acids by CE are rather rare (Tables 7-8). The objective of the present paper is to summarize and discuss the different procedures used in CE for the separation of short chain organic acids and aromatic containing ones, and underline the advantages versus the drawbacks of sensibility and selectivity of the different parameters used: composition of carrier electrolyte, pH, ionic strength, electro-osmotic flow modifier, additives of metal ions and organic solvent. The separation, injection and detection modes are also discussed.

Table 1. Formulas and some properties of some aliphatic and aromatic acids.

Usual Name	IUPAC name	Graphic formulas	M_r, g/mol	pK_a	Solubility
Aliphatic					
Formic	methanoic		46.03	3.75	miscible
Acetic	ethanoic		60.05	4.76	fully miscible
Oxalic	ethanedioic		90,03	1.27 4.27	10 g/100 ml (20°C)
Tartaric	2,3-dihydroxybutanedioic		150.1	3.04 4.37	20,6 g/100 ml (20°C)
Citric	2-hydroxy-1,2,3-propanetricarboxylic		192.13	3.15 4.77 6.40	133 g/100 ml
Aromatic					
Benzoic	benzenmonocarboxylic		122.12	4.18	0,27 g/100 ml (18°C)
Phtalic	Benzene-1,2-dicarboxylic		164.14	2.95 5.41	0,57 g/100 ml (20°C)
Isophtalic	Benzene-1,3-dicarboxylic		164.14	3.62 4.6	0,013 g/100 ml (25°C)
Terephtalic	Benzene-1,4-dicarboxylic		164.14	3.54 4.46	0,0016 g/100 ml
Trimellitic	Benzene-1,2,4-tricarboxylic		210.14	2.5 3.8 5.2	
Trimesic	Benzene-1,3,5-tricarboxylic		210.14	2.9 3.9 4.7	
Pyromellitic	Benzene-1,2,4,5-tetracarboxylic		254.15	1.9 2.9 4.5 5.6	
Mellitic	Benzene-hexacarboxylic		342.17	0.8 2.26 3.52 5.15 6.52	

2. Method development parameters

2.1 Separation mode

Negatively charged species such as anions of organic acids can be separated in a co-electro-osmotic mode (identical directions of electro-osmotic and electrophoretic velocity, anodic mode) or in a counterelectro-osmotic mode (opposite directions of electro-osmotic and electrophoretic velocity, cathodic mode). The electro-osmotic flow (EOF) normally oriented towards the cathode (cathodic mode). In order to establish co-electro-osmotic conditions the EOF direction has to be reversed (anodic mode). That aim is achieved using an electro-osmotic flow modifier as ruler cationic surfactant. In most of works dealing with the determination of organic acid anions, co-electro-osmotic mode is used (Tables 2-8). An exception is made of the cases when a simultaneous separation of cations and anions is needed [5, 6], or ion-pairing the EOF modifier with solute and precipitation of surfactant salts [7, 8] are possible. Co-electro-osmotic conditions lead to short analysis times. However in that case the time window available for separation is limited by the migration time of the neutral marker corresponding to the last peak in the electropherogram. That is also reason why the co-electro-osmotic mode might be better suited for the analysis of organic anions which have large mobilities, such as oxalate, acetate, and formate.

2.2 Injection mode

At one capillary end, the background electrolyte reservoir is replaced by the sample reservoir only during sample injection. Two injection modes are usually applied: either hydrodynamic or electrokinetic (electromigration) injection. It is noted in [9], that electrokinetic injection involves biases. When a voltage is applied to the capillary length during elektrokinetic injection, a larger effective volume of faster ions

than slower ions will be injected, because of the different mobilities of the species in the sample solution. Contrary to electrokinetic injection, hydrodynamic injection is based on pressure or gravity and does not discriminate between the ions. Hence the same effective sample volume of each ion is injected. Hydrostatic injection is also relatively independent of sample matrix effects [10]. However it is noted in [11, 12], that owing to the small injection volume and the low concentration of the sample, the detection limit for the hydrostatic injection is relatively high. It is therefore not recommended to use this method for trace analysis. Electrokinetic injection as a preconcentration method allows an improvement of the detection limit of fast analyte ions by a factor of 15 [11]. However disadvantages of the latter method are: the discrimination against ions having a low mobility, the dependence of the enrichment factor on the conductivity of the sample and the necessity of a correcting calculation using two internal standards. Thus hydrodynamic injection is more often used than electrokinetic one (Tables 2-8).

The selection of the injection time is based on the relative standard deviations for peak area. They were found to decrease with increasing injection time. In order to obtain high resolution in CE, the volume of the injected sample must be small compared with the capillary volume.

With the aim of increasing the sensitivity of determination, sample stacking is sometimes used [10] in both the hydrodynamic and electrokinetic injection modes. The principles, advantages and limitations of such method have been reviewed in [13, 14]. Sample stacking results from the movement of sample ions across a boundary that separates the region containing the sample ions from the rest of the capillary containing the background buffer solution. The region containing the sample ions is a low conductivity solution while the background region is a high conductivity

solution. If low and high conductivity solutions are present inside a capillary upon application of voltage, the low conductivity region will experience a higher electric field compared to the background region. Sample ions will then move faster in the low conductivity region than in the high conductivity region. Thus sample ions will be concentrated in the boundary between low and high conductivities regions.

The stacking effect, for example, was used in work [15] for the measurement of the short chain organic acids (formic, acetic, oxalic and citric) in natural latex serum. In this case, a large-volume injection of sample solutions prepared in low conductivity matrices containing 50 % acetonitrile (w/v) and 0,5 % NaCl (w/v) was used; That resulted in enhancement factors over 17. In paper [16] stacking enrichment was used for the determination of formate, acetate and oxalate in rain waters. With 10 % filling of the capillary (which corresponds to a sample volume of about 300 nl) extremely small detection limits can be reached. With a higher sample volume, the baseline noise has an excessively high level.

3. Detection mode

Photometric detection is widely used In capillary electrophoresis (Tables 2-8). Short-chained carboxylic acids are known to be of lack of chromophore groups. The only present chromophore group is the carboxylic group. It absorbs weakly and presents its maximum absorbance around 200 nm. So, direct UV-detection is not often used, except in works [17-22]. Their authors employed UV-detection at 185 nm. In the works [15, 23-25] that was done at 200 nm. Direct detection is not as sensitive as the indirect mode in the case of the short chain organic acids. Consequently the latter mode has been used by most authors. In that mode of detection, an absorbing ionic species is added to the carrier electrolyte. These species has the same charge as the analyte of interest. In this case, the sensitivity depends on the difference of

absorption of analyte (if it absorbs) and that of the counter ion in the run buffer. The use of this type of detection was reviewed in [26]. The impacts of some factors are discussed. As the indirect photometric detection method is widely used, the authors of most works pay special attention to the choice of an absorbing co-ion as the principal component of the background electrolyte. The most popular chromophores used for the determination of organic acid anions are as follows: inorganic chromophore: chromate (254 nm) [11, 27-30], molybdate (230 nm) [12], aromatic acids with strong UV chromophores: phtalic, trimellitic, pyromellytic, benzoic. In work [16], the aminobenzoic acids were used. In works [31-33], pyridinedicarboxylic acid is proposed also for this aim. The sensitivity of this mode of detection is 2-3 orders higher in magnitude than the direct one (Tables 2-8).

The electrochemical detection in CE may be a good alternative to UV indirect detection for carboxylic acids. The detectors can be classified into those measuring a bulk property of the solution (conductivity) and those measuring signals due to phenomena at the interface between a solid electrode and solution. Some works have paid attention for the development of conductivity [34-38], potentiometric [5] and amperometric [39, 40] detection. The distinct advantage of conductivity detection is that the response of the detector is directly related to the ionic mobility of the species under detection. This confers on conductivity detection, in CE, an unique advantage since the use of an internal standard allows an accurate determination of the absolute concentration of each component in a mixture without separate calibration of response for each component [34]. It is noted in [38, 41], that conductivity detection proved to be more sensitive and to offer significant enhancement in performance for the faster migrating low-molecular-mass anions (oxalate, formate). Different modes of conductivity detection are used: on-column [34] and end-column

detection [35], nonsuppressed [38] or suppressed [36] conductivity detection to overcome high background noise and electrical field interferences. In the case of “end-column” conductimetric detection, a sensing microelectrode is placed at the outlet of the fused-silica capillary. In this manner, it does not suffer from electrical interference caused by the applied high voltage during the CE separation. In the case of suppressed conductivity detection, a conversion of the conductive buffer to a weakly conducting solution before it entered the conductivity detector is used, thus lowering the background conductivity and the noise levels. As a converter, ion-exchange membrane is used.

However, this type of detection is not yet widely used for carboxylic acid determination. Some carboxylic acids are not electroactive, so direct potentiometric or amperometric detection is not possible. The technical problem to combine CE with electrochemical detector has also arisen. The advantages and drawbacks of this type of detection are discussed in the reviews [42, 43].

The application of other methods of detection has also been demonstrated. An example is mass spectrometry, which is used for the determination of acetate [44]. Another example is indirect laser induced fluorescence with flavin mononucleotide. It is employed in the determination of formate, oxalate, tartrate and citrate [45]. However these types of detection are very expensive. Hence they are rarely used in practice.

4. Optimization of the carrier electrolyte composition

4.1 Mobility of the carrier electrolyte

In CE the peak shape is strongly influenced by the difference in mobility between the carrier electrolyte and the solutes. Optimal results can be obtained by the use of carrier electrolyte with an electrophoretic mobility as close as possible to

that of the analytes under investigation. In theory, the background electrolyte (BGE) with mobility matching those of the majority of the analytes would give a better separation and resolution. The electrophoretic mobilities for the various BGEs under consideration decrease in the following order [12, 46] (Fig. 1): chromate > pyromellitate (PMA) > trimellitate (TMA) > terephtalate, phthalate > benzoate > p-hydroxybenzoate (PHBA). Chromate has the highest mobility, and is most suitable as the BGE for rapid anions. However, for the slower moving organic acids (like acetate or benzoate), performing CE using chromate as the BGE results in poor resolution and trails. Other ionized BGEs from pyromellitate to benzoate, since their absorbtion characteristics are similar, are equally chosen for the separation of short chain organic acids. The Tris [12, 47] or His [37, 41] buffer was often added to the BGE to provide stabilization against pH change and to reduce the baseline noise.

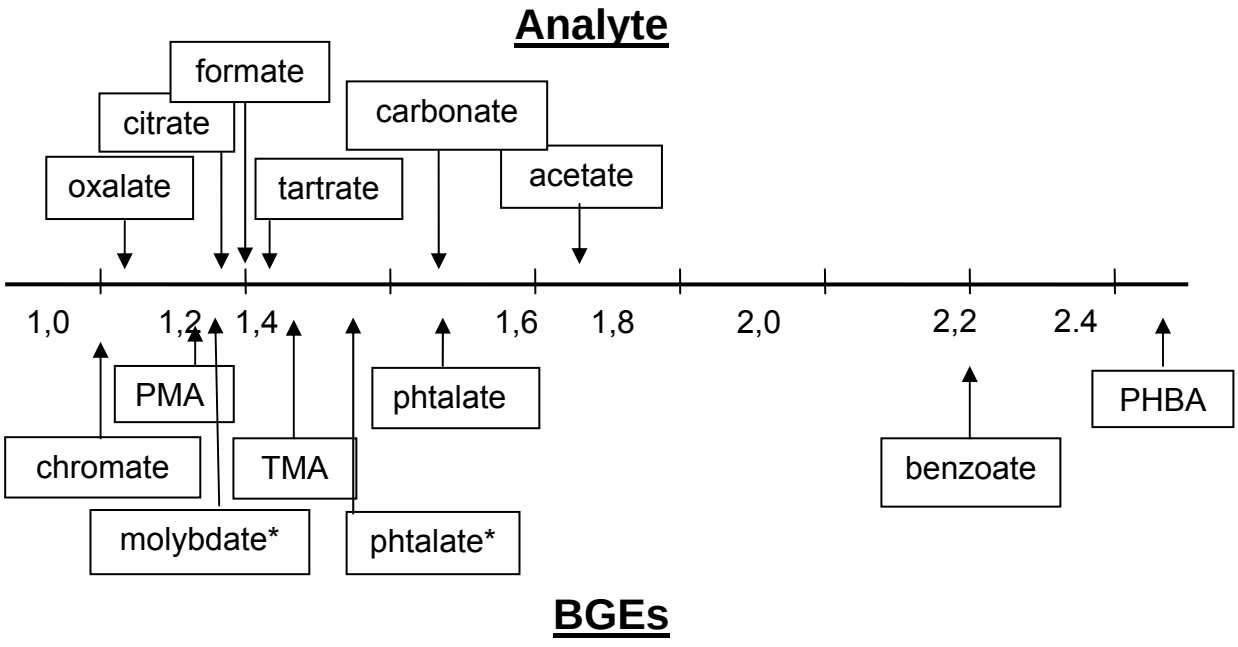


Figure 1. Relative electrophoretic mobilities (with respect to chromate) of several BGEs and organic anions at pH 8,0 [46] and at pH 11,0 (*) [12].

Regarding the separation of a mixture of carboxylic acids, a compromise must be found to achieve satisfactory peak shape for all analytes under investigation. Polyprotic inorganic acids such as boric [19, 22, 36] or phosphoric [15, 17, 20, 21, 23-25] acid have proved to be useful also for this purpose. These carrier electrolytes allow the separation of a number of organic acids covering a wide range of electrophoretic mobilities without major loss in peak shape. But it is necessary to note that sensitivity in the case of weakly absorbing organic acids (formic, acetic, oxalic) is not elevated.

4.2 Effect of ionic strength

An often overlooked effect is the influence of the ionic strength of the carrier electrolyte upon the separation selectivity. As ionic strength decreases, lower peak efficiency is observed. This effect can be explained in terms of the ratio of sample concentration to carrier electrolyte concentration. In order to obtain a high resolution separation of closely migrating peaks, the concentration of the injected sample must be kept low relative to the electrolyte. To attain higher efficiency with samples of high concentration, the concentration of the electrolyte must be increased in order to maintain a large ratio of electrolyte concentration to sample band concentration. In other side, the current observed for a given applied voltage is proportional to the ionic strength of electrolyte. If it overcomes a certain value, heating due to Joule effect becomes difficult to be dissipated. This effect, manifested as noise and baseline aberrations, is enhanced by the use of a highly absorbing carrier ion for indirect UV detection. For this reason, the ionic strength must be minimized to prevent noise resulting from high current [48]. So, the optimum ionic strength must be balanced between acceptably low current, to minimize noise, and good peak efficiency.

Generally, for indirect photometric detection, the ionic strength of the spectroscopic buffer is relatively low, between 5 and 20 mM (Tables 2-8), in order to decrease baseline noise. For a direct detection, ionic strength as high as 500 mM can be used [15, 49], if high ionic strength sample must be analyzed with minimal dilution.

4.3 Effect of pH

The pH of the run buffer affects the degree of ionization of the anions and their mobilities. At low pH, anions may become protonated, causing a decrase in their charge-to-size ratio with subsequent decrease in their mobilities. As the pH is raised, their mobilities increase and their migration times get shorter. In acidic media, the pH value affects the di-, tri- and tetraprotonic acids most significantly. In the case of monocarboxylic acids, their electrophoretic mobilitiy decreases when their ionic radius increases.

At pH about 3-6, most of the acids of interest (Table 1) are affected by pH changes. Variation of the pH is the most common approach to optimise separation selectivity of organic acids [46, 50-52].

4.4 Electroosmotic flow modifier

For the separation of anions, coelectroosmotic mode is widely used. Since the analytes migrate towards the anode in the opposite direction to the electroosmotic flow, adding cationic surfactants or alkylamines tends to neutralize the negative surface charges on the bare fused-silica capillary, thus reducing the electroosmotic flow. These compounds are often called electroosmotic flow modifiers. Further, when enough modifiers are added to the running buffer, the direction of the electroosmotic flow can be reversed, further facilitating the migration of anions. The migration time of anions can thus be shortened significantly.

A variety of alkyl ammonium salts have been used as flow modifiers, including cetyltrimethylammonium bromide (CTAB) [15, 23-25, 53, 54] or hydroxide (CTAH) [12], tetradecyltrimethylammonium bromide (TTAB) [11, 17, 22, 34, 35, 37, 41, 46, 50, 55, 56] or hydroxide (TTAH) [16], amines, such as diethylentriamine (DETA) [57, 58]. It is noted [12], that CTAH is more effective to reverse the EOF than TTAH due to its longer alkyl chain. Most of above mentioned flow modifiers have been found to be compatible with analytes and other electrolyte components. One disadvantage of hydrophobic alkylammonium salts, such as CTAB and TTAB, is their limited solubility and tendency to form insoluble pairs with some electrolyte components [48]. To overcome this problem, hexamethonium salt was proposed [48]. The hexamethonium ion is very effective in reversing electroosmotic flow, is highly soluble, and does not interact with other electrolyte components. In addition, because hexamethonium is a quaternary ammonium, its ability to modify the wall of the capillary is not changed as a function of pH, a phenomenon that could otherwise leads to unstable electroosmotic flow. Another quaternary ammonium salt such as myristyltrimethylammonium bromide (MTAB) [21] was also proposed.

It follows to note that it is desirable to have only one carrier anion in the electrolyte in the case of indirect detection. The presence of other anions can lead to baseline aberrations and a decrease in sensitivity [48]. The use of bromide salts of quaternary amines as flow modifiers causes a dip in the baseline at the migration time corresponding to bromide peak when indirect UV detection is used for the analysis of anions. This phenomenon has also been observed with sulphate and chloride when these anions are added to the electrolyte. Because the presence of small amount of hydroxide ion in the buffer does not cause these problems, it is better to convert the chloride or bromide salts of amines to the hydroxide form. Unlike

bromide and chloride counterions, the addition of small amounts of hydroxide to the electrolyte solution has no adverse effect on the separation or detection of anions.

4.5 Other additives

Change in the mobility of organic acids is often achieved by the use of various buffer additives. Complex-forming agent like alkaline earth cations [16, 36, 47, 51, 59, 60], divalent transition metal cations (Co(II), Ni(II), Cu(II)) [61] or cyclodextrines [59] which influence the charge/ionic radius ratio of the analytes as well as organic solvents which affect the ionic solvation and dissociation are used for these purposes [52].

Addition of alkaline earth metal ions to the carrier electrolyte is an efficient way to optimize the separation of organic acids. The change in the migration behaviour of the solutes caused by complex formation becomes more pronounced if the stability of the analyte-metal complex increases. Therefore separations can be achieved for the analytes showing different stability constants with metal ions. Structural attributes of the solutes play also an important role in the formation of these complexes; it was demonstrated that, in the case of di- and polycarboxylic acids, the mobilities of analytes carrying carboxylate groups were distinctly more influenced by a complex formation with Ba(II) ions than the other solutes [59]. Additional to effect discussed above, these cationic additives significantly decrease the EOF because of the partial neutralization of the negative charge of silanol groups on the inner surface of the capillary. However in work [47] it is noted that, if the sulphate concentration is too high in the sample, insoluble salts with Ca(II) or Ba(II) can be formed resulting in a non-linear calibration.

Another group of additives used for the analysis of low-molecular-mass organic acids are compounds such as cyclodextrine which can form inclusion

complexes with these analytes. It should be emphasized that inclusion complexes may also be formed with components of the carrier electrolyte such as EOF modifiers. Eventually, coelectrosmotic separation conditions for organic acids may be reversed into counterelectroosmotic conditions upon addition of cyclodextrines. Cyclodextrines were employed for the separation of aromatic and aliphatic carboxylic acids [59].

Another possibility to modify the migration behaviour of organic acids is the addition of organic solvents to the carrier electrolyte. In addition to improving the solubility of hydrophobic analytes, these additives have an influence on the degree of dissociation as well as solvation of the solutes and the EOF. Generally the addition of organic solvents leads to a decreased EOF and thereby to increased separation times. Triethanolamine was used in [48] for the separation of a number of inorganic and organic (formate, phthalate) cations. 0,01 % PVA was used as an additive for anion analysis in rainwater (acetate, formate) [12]. In reference [49], methanol was used for the improvement of the separation of organic acids (oxalic, acetic) in urine. In order to separate a number of phenolic and dicarboxylic acids (between them phtalic, benzoic, oxalic) in beer samples with high separation efficiencies, organic solvent as 2-propanol was used [62].

5. Applications

CE is extensively used now for the determination of organic acids in real samples, especially with complex composition, in particular, in industrial products, biological, food and environmental samples. These applications were reviewed in [52, 63, 64]. Compared to chromatographic techniques, CE was proved to be advantageous, especially in the case of problematic matrices, because this technique does not depend on chromatographic columns and stationary phases which may be

deteriorated by such samples. Therefore, a complicated sample pretreatment is not always needed. On the other hand, CE provides a separation mechanism which results in a selectivity distinctly different from that of other chromatographic techniques used in the analysis of organic acids.

6. Conclusion

CE is a perspective method for the analysis of carboxylic acids. The spectrophotometric mode is widely used to detect these species. Indirect mode is preferable for detection of formic, acetic, oxalic, tartaric and acetic acids as these species do not absorb (or absorb little) in UV-visible range. On the contrary, direct detection is preferred for the determination of aromatic acids (benzoic and phtalic), because these acids absorb well in the UV range. So it seems that the conductometric detection is more desirable in the case of a simultaneous determination of mono-, di- carboxylic and aromatic acids. And, as a ruler, the conductometric detection is more sensitive.

In the literature, there is a lack of data on the determination of some aromatic acids of interest like mellitic, trimellitic and trimesic by CE. Only one paper devoted to the separation and determination of trimelitic and trimesic acids was found [59]. This application of CE appears as a relatively new area.

Table 2. CE determination conditions and detection limits for formate

Detection mode	Buffer	pH	Additives	DL, M	Ref.
I. Spectroscopic					
1.1 Photometric					
1.1.1 Direct					
185 nm	tetraborate, 50 mM	10	OFM[a]	1×10^{-4}	[19]
	phosphate, 25 mM	7	0,5 mM TTAB	2×10^{-5}	[17]
200 nm	phosphate, 500 mM	6,25	0,5 mM CTAB	$1,6\times10^{-3}$	[15, 23-25]
1.1.2 Indirect					
210 nm	phtalate, 5 mM	7	0,25 mM CTAB		[54]
214 nm	NDS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	9×10^{-7} **	[58]
	NTS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	$4,3\times10^{-7}$ **	[58]
	nicotinate, 4 mM/ creatinine, 15 mM	5,37	*		[8]
220 nm	pyromellitate, 3 mM	7,5	3 mM DETA	1×10^{-6}	[57]
	trimellitate, 5 mM	9	1 mM TTAB	$\sim2\times10^{-6}$	[46]
230 nm	salycylate, 7,5 mM /TRIS,15 mM	8,1	0,4 mM DoTAH, 1,05 mM Ca(II), 0,6 mM Ba(II)		[47]
	molybdate, 5mM/ TRIS	7,9	0,15 mM CTAH, 0,01% PVA		[12]
250 nm	pyromellitate, 2,5 mM	7,7	0,75 mM HMH, 1,6 mM triethanolamine		[48]
254 nm	chromate, 5 mM	10	OFM[a]		[30]
	chromate, 5 mM	8	OFM[a]		[27]
	chromate, 6 mM	8	OFM[a]	2×10^{-6}	[29]
	phtalate, 5mM	5,6	OFM[a]		[30]
	phtalate, 5mM	5,6	OFM[a], 0,2-0,6 mM Ca(II)		[60]
	phtalate, 15mM	5,6	0,6 mM TTAB	$2,2\times10^{-7}$***	[56]
	benzoate, 10 mM	6	OFM[a]		[30]

	4-hydroxybenzoate, 5mM	4,75	OFM[a], 0,4 mM Ca(II)		[51]
	p-AB, 7,5 mM/HIS	5,75	0,12 mM TTAB	$2{,}4\times10^{-6}$	[37]
	PDC, 9mM	7,8	0,5 mM TTAB	$6{,}5\times10^{-6}$	[55]
	PyDC, 10mM	12	OFM[a]		[65]
264 nm	p-AB, 7,5 mM	9,6	55 μM TTAH, 0,76 Ba(II)	3×10^{-8}**	[16]
275nm	chromate, 10 mM		2 mM TTAOH		[66]
280 nm	NDC, 2 mM	8-11	0,5 mM TTAB	3×10^{-6}	[50]
314 nm	indigo-tetrasulfonate, 500mM/ BIS-TRIS, 2,67 mM	6,8	*	5×10^{-7}	[67]
350nm					
with reference 230 nm	PDC, 20 mM	5,7	0,5 mM CTAH		[32]
with reference 230 nm	PDC, 20 mM	12,1	0,5 mM CTAH		[33]
with reference 200 nm	PDC, 5 mM	5,6	0,5 mM CTAB	$1{,}5\times10^{-5}$	[31]
1.2 LIF					
Indirect	30 μM flavin mononucleotide/ boric acid, 100 mM	8	2 mM DETA	$\sim4\times10^{-7}$	[45]
II. Electrochemical					
2.1. Conductometric	MES, 10 mM /His	6	0,2 - 0,5 mM TTAB		[34]
	MES, 20 mM/His	6	1 mM TTAB		[35]
	tetraborate, 2 mM	9,2	*0,02 mM Ba(II)		[36]
	CHES, 50 mM/arginine,30 mM	9			[38]
	p-AB, 7,5 mM/ HIS	5,75	0,12 mM TTAB	7×10^{-7}	[37]
2.2 Potentiometric	HEPES, 5 mM	7,6	*	$\sim1\times10^{-6}$	[5]
III. Simultaneous					
UV Indirect at 254 nm and Conductivity	p-AB,7,5 mM/ HIS	5,75	0,12 mM TTAB	$\sim2{,}4\times10^{-6}$(UV) $\sim7\times10^{-7}$(c)	[37, 41]

*a – commercial products, b – pretreated column, * coelectrosmotic mode, ** with stucking, *** electrokynetic injection, DL – detection limit.*

Table 3. CE determination conditions and detection limits for acetate

Detection mode	Buffer	pH	Additives	DL, M	Ref.
I. Photometric					
1.1 Direct					
185 nm	tetraborate, 50 mM	10	OFM[a]	8×10^{-5}	[19]
	phosphate, 25 mM	7	0,5 mM TTAB	1×10^{-5}	[17]
	phosphate, 3 mM	6,5	0,5 mM MTAB	3×10^{-6}	[21]
	phosphate, 10 mM/ tetraborate, 5mM	3,9	0,001 % HDB	5×10^{-5}	[18]
200 nm	tetraborate, 50 mM	9,2	2,5 % TTAB		[22]
	phosphate, 500 mM	6,25	0,5 mM CTAB	$1,77\times10^{-4}$ 5×10^{-3}	[15, 23-25]
1.2 Indirect					
200 nm	PDC, 5 mM	5,6	0,5 mM CTAB	3×10^{-5}	[53]
210 nm	phtalate, 5 mM	7,0	0,25 mM CTAB		[54]
	1,2-dimethylimidazole, 4mM/ trimellitate, 1,0 mM	7,0	*	$1,3\times10^{-6}$	[6]
214 nm	nicotinate, 4 mM /creatinine,15 mM	5,0-5,4	*		[8]
220 nm	pyromellitate, 3 mM	7,5	3 mM DETA	1×10^{-7}	[57]
	trimellitate, 5 mM	9,0	1 mM TTAB	$\sim2\times10^{-6}$	[46]
230 nm	molybdate, 5 mM/TRIS	7,9	0,15 mM CTAH, 0,01% PVA	2×10^{-5}	[12]
	salycylate, 7,5 mM /TRIS,15 mM	8,1	0,4 mM DoTAH, 1,05 mM Ca(II), 0,6 mM Ba(II)		[47]
254 nm	chromate, 5 mM	10,0	OFM[a]		[30]
	chromate, 5 mM	8,1	0,01 mM TTAB		[11]
	chromate, 5 mM	8,0	OFM[a]		[27]
	chromate, 6 mM	8,0	OFM[a]	$1,5\times10^{-6}$	[29]
	chromate		OFM[a]		[28]
	phtalate, 15 mM	5,6	0,6 mM TTAB	$1,7\times10^{-7***}$	[56]
	phtalate, 5 mM	5,6	OFM[a]		[30]
	phtalate, 5 mM	5,6	OFM[a], 0,2-0,6 mM Ca(II)		[60]
	benzoate, 10 mM	6,0	OFM[a]		[30]
	4-hydroxybenzoate, 5 mM	4,75	OFM[a], 0,4 mM Ca(II)		[51]

	PDC, 9 mM	7,8	0,5 mM TTAB	$6,7\times10^{-6}$	[55]
	PyDC, 10 mM	12,0	OFM[a]		[65]
	nitroso-R salt, 0,5 mM	8,0	*	2×10^{-5}	[68]
	126NNS, 0,5 mM	8,0	*	2×10^{-5}	[68]
	216NNS, 0,5 mM	8,0	*	2×10^{-5}	[68]
264 nm	p-AB, 7,5 mM	9,6	55 µM TTAH, 0,76 mM Ba(II)	2×10^{-8}**	[16]
280 nm	NDC, 2 mM	8-11	0,5 mM TTAB	2×10^{-6}	[50]
350 nm					
with reference 230 nm	PDC, 20 mM	5,7	0,5 mM CTAH		[32]
with reference 230 nm	PDC, 20 mM	12,1	0,5 mM CTAH		[33]
with reference 200 nm	PDC, 5 mM	5,6	0,5 mM CTAB	2×10^{-5}	[31]
II. Electrochemical					
2.1. Conductometric					
	MES/HIS,10 mM	6	0,2 - 0,5 mM TTAB		[34]
	MES/HIS, 20 mM	6	1 mM TTAB		[35]
	CHES, 50 mM/arginine,30 mM	9			[38]
	tetraborate, 2 mM	9,2	*0,02 mM Ba(II)		[36]
2.2 Potentiometric	HEPES, 5 mM	7,6	*	$\sim1\times10^{-6}$	[5]
III. Simultaneous					
UV Indirect at 254 nm and Conductivity	p-AB, 7,5 mM /HIS	5,75	0,12 mM TTAB	$\sim2\times10^{-6}$(UV) $\sim2\times10^{-6}$(c)	[37, 41]

*a – commercial products, b – pretreated column, * coelectrosmotic mode, ** with stucking, *** electrokynetic injection, DL – detection limit.*

Table 4. CE determination conditions and detection limits for oxalate

Detection mode	Buffer	pH	Additives	DL, M	Ref.
I. Spectroscopic					
1.1 Photometric					
1.1.1 Direct					
185 nm	tetraborate, 25 mM	9-10	0,5 mM TTAB, 2,25mM Ba(II), 2 mM β-cyclodextrin		[59]
	tetraborate, 50 mM	10	OFM[a]	6×10^{-5}	[19]
	phosphate, 25 mM	7	0,5 mM TTAB	5×10^{-6}	[17]
	phosphate, 15 mM	10,1	OFM[a]	$2,7\times10^{-6}$	[69]
200 nm	tetraborate, 50 mM	9,2	2,5 % TTAB		[22]
	phosphate, 500 mM	6,25	0,5 mM CTAB	2×10^{-5}	[15, 23-25]
	phosphate, 200mM	6	100 mL/L methanol[a]		[49]
210 nm	phosphate, 50 mM	8	0,001 % HDB, 25 % 2-propanol	1×10^{-5}	[62]
1.1.2 Indirect					
210 nm	phtalate, 5 mM	7	0,25 mM CTAB		[54]
	1,2-dimethylimidazole, 4 mM/ trimellitate, 1,0 mM	7	*	1×10^{-5}	[6]
214 nm	NDS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	$6,1\times10^{-7}$ **	[58]
	NTS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	$4,4\times10^{-7}$ **	[58]
220 nm	pyromellitate, 3 mM	7,5	3 mM DETA	1×10^{-6}	[57]
	trimellitate, 5 mM	9	1 mM TTAB	$\sim2\times10^{-6}$	[46]
230 nm	salycylate, 7,5 mM /Tris,15 mM	8,1	0,4 mM DoTAH, 1,05 mM Ca(II), 0,6 mM Ba(II)		[47]
	carbonate,5 mM/phtalate,1,5 mM	7	[b]		[70]
254 nm	chromate, 6 mM	8	OFM[a]	1×10^{-6}	[29]
	chromate, 5 mM	10	OFM[a]		[30]
	chromate, 5 mM	8,1	0,01 mM TTAB	3×10^{-8}**	[11]

	chromate, 10 mM	8	0,5 mM TTAB, 0,1 mM EDTA	3×10^{-6}	[71, 72]
	chromate, 10 mM	8,1	0,5 mM TTAB	$7,8\times10^{-5}$	[73]
	phtalate, 5mM	5,6	OFM[a], 0,2-0,6 mM Ca(II)		[60]
	phtalate, 15mM	5,6	0,6 mM TTAB		[56]
	PDC, 9mM	7,8	0,5 mM TTAB	$3,3\times10^{-6}$	[55]
	PyDC, 10mM	12	OFM[a]		[65]
	4-hydroxybenzoate, 5mM	4,75	OFM[a]0,4 mM Ca(II)		[51]
	Nitroso-R salt, 0,5 mM	8	*	1×10^{-5}	[68]
	126NNS, 0,5 mM	8	*	1×10^{-5}	[68]
	216NNS, 0,5 mM	8	*	1×10^{-5}	[68]
264 nm	p-AB, 7,5 mM	9,6	55 μM TTAH, 0,76 Ba(II)	$2\times10^{-8**}$	[16]
275nm	chromate,10 mM		2 mM TTAOH		[66]
350nm					
with reference 230 nm	PDC, 20 mM	5,7	0,5 mM CTAH		[32]
with reference 230 nm	PDC, 20 mM	12,1	0,5 mM CTAH		[33]
with reference 200 nm	PDC, 5 mM	5,6	0,5 mM CTAB	2×10^{-5}	[31]
1.2 LIF					
Indirect	30 μM flavin mononucleotide/ boric acid, 100 mM	8	2 mM diethylenetriamine	$\sim2\times10^{-7}$	[45]
II. Electrochemical					
2.1. Conductometric	CHES, 50 mM/arginine,30 mM	9			[38]
2.2 Amperometric	phosphate, 15 mM	6,2–7	0,2 mM CPB	1×10^{-6}	[40]
III. Simultaneous					
UV Indirect at 254 nm and Conductivity	p-AB,7,5 mM/HIS	5,75	0,12 mM TTAB	2×10^{-6}(UV) $4,5\times10^{-7}$ (c)	[37],[38]

Table 5. CE determination conditions and detection limits for tartrate.

Detection mode	Buffer	pH	Additives	DL, M	Ref.
I. Spectroscopic					
1.1 Photometric					
1.1.1 Direct					
185 nm	phosphate, 3 mM	6,5	0,5 mM MTAB	9×10^{-7}	[21]
200 nm	phosphate, 200 mM	7,5	*	$1,3\times10^{-5}$	[74]
1.1.2 Indirect					
200 nm	PDC, 5 mM	5,6	0,5 mM CTAB	$1,3\times10^{-4}$	[53]
210 nm	1,2-dimethylimidazole, 4 mM/trimellitic acid, 1,0 mM	7	*	$1,3\times10^{-6}$	[6]
214 nm	NDS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	2×10^{-7} [c]	[58]
	NTS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	3×10^{-7} [c]	[58]
220 nm	pyromellitate, 3 mM	7,5	3 mM DETA	$1,2\times10^{-6}$	[57]
	trimellitate, 5 mM	9	1 mM TTAB	$\sim2\times10^{-6}$	[46]
230 nm	carbonate, 5mM / phtalate, 1,5 mM	7	[b]	7×10^{-6}	[70]
254 nm	chromate		OFM[a]		[28]
	phtalate, 5mM	5,6	OFM[a] 0,2-0,6 mM Ca(II)		[60]
	phtalate, 15mM	5,6	0,6 mM TTAB	$5,3\times10^{-8***}$	[56]
260 nm	benzoic acid,12 mM/ histidine, 10 mM	5	1 mM TTAB		[75]
264 nm	4-aminobenzoate, 7,5 mM	9,6	55 μM TTAH, 0,76 Ba(II)	$3\times10^{-8**}$	[16]
314 nm	indigo-tetrasulfonate, 500mM/ BIS-TRIS, 2,67 mM	6,8	*	1×10^{-7}	[67]
350nm					
with reference 230 nm	PDC, 20 mM	5,7	0,5 mM CTAH		[32]
with reference 230 nm	PDC, 20 mM	12,1	0,5 mM CTAH		[33]

1.2 LIF					
Indirect	30 μM flavin mononucleotide/ boric acid, 100 mM	8	2 mM diethylenetriamine	$\sim 1\times10^{-7}$	[45]
II. Electrochemical					
2.1. Conductometric	tetraborate, 2 mM	9,2	0,02 mM Ba(II)		[36]
2.2 Amperometric	NaOH, 0,05 mM		0,2 mM CTAB	7×10^{-7}	[76]
	phosphate, 15 mM	7	0,2 mM CPB	$5,5\times10^{-6}$	[40]

*a – commercial products, b – pretreated column, * coelectrosmotic mode, ** with stucking, *** electrokynetic injection*

Table 6. CE determination conditions and detection limits for citrate.

Detection mode	Buffer	pH	Additives	DL, M	Ref.
I. Spectroscopic					
1.1 Photometric					
1.1.1 Direct					
185 nm					
	tetraborate, 50 mM	10	OFM[a]	3×10^{-5}	[19]
	phosphate, 25 mM	7	OFM[a]		[20]
	phosphate, 15 mM	10,1	OFM[a]	$2{,}3\times10^{-6}$	[69]
	phosphate, 10 mM/ tetraborate, 5 mM	3,9	0,001 % polybrene	$8{,}3\times10^{-6}$	[18]
200 nm	phosphate, 200 mM	7,5	*	1×10^{-5}	[74]
	phosphate, 200mM	6	100 mL/L methanol[a]		[49]
	phosphate, 500 mM	6,25	0,5 mM CTAB	$1{,}6\times10^{-4}$	[15, 23-25]
1.1.2 Indirect					
214 nm	NDS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	$2{,}1\times10^{-7}$ **	[58]
	NTS, 4mM/ boric acid,100 mM/ tetraborate,5 mM	8	2 mM DETA	$2{,}3\times10^{-7}$ **	[58]
220 nm	pyromellitate, 3 mM	7,5	3 mM DETA	2×10^{-6}	[57]
	trimellitate, 5 mM	9	1 mM TTAB	$\sim2\times10^{-6}$	[46]
	ε-aminocaproic acid, 10 mM/ mandelic acid,10 mM	3,8	*	8×10^{-6}	[77]
230 nm	5 mM carbonate/1,5 mM phtalate	7,0	[b]	8×10^{-6}	[70]
	electrolye containing trimesic acid*		*	$\sim5\times10^{-7}$	[78]
254 nm	chromate		OFM[a]		[79]
	chromate		OFM[a]		[28]
	chromate	8,0	OFM[a]		[80]

	chromate, 5 mM	8,0	OFM[a]		[27, 81]
	chromate, 10 mM	8,0	0,5 mM TTAB, 0,1 mM EDTA		[72]
	chromate, 10 mM	8,1	0,5 mM TTAB	$3{,}6\times10^{-5}$	[73]
	phtalate, 15mM	5,6	0,6 mM TTAB	$4{,}2\times10^{-7***}$	[56]
	p-AB, 7,5 mM/His	5,75	0,12 mM TTAB	1×10^{-6}	[37]
	4-hydroxybenzoate, 5mM	4,75	OFM[a], 0,4 mM Ca(II),		[51]
264 nm	p-AB, 7,5 mM	9,6	55 µM TTAH, 0,76 Ba(II)		[16]
314 nm	0,5 mM indigo-tetrasulfonate/ 2,67 mM BiS-TRIS	6,8	*	2×10^{-5}	[67]
350 nm					
with reference 230 nm	PDC, 20 mM	5,7	0,5 mM CTAH		[32]
with reference 230 nm	PDC, 20 mM	12,1	0,5 mM CTAH		[33]
1.2 LIF					
Indirect	30 µM flavin mononucleotide/ boric acid, 100 mM	8,0	2 mM diethylenetriamine	$\sim1\times10^{-7}$	[45]
II. Electrochemical					
2.1. Conductometric	p-AB, 7,5 mM/HIS	5,75	0,12 mM TTAB	$5{,}3\times10^{-7}$	[37]
	tetraborate, 2 mM	9,2	0,02 mM Ba(II)		[36]
2.2 Amperometric	phosphate, 15 mM	6,27	0,2 mM CPB	5×10^{-7}	[40, 82]
III. Simultaneous					
UV Indirect at 254 nm and Conductivity	7,5 mM 4-aminobenzoic acid/His	5,75	0,12 mM TTAB	1×10^{-6}(UV) $5{,}3\times10^{-7}$(c)	[37]

*a – commercial products, b – pretreated column, * coelectrosmotic mode, ** with stucking, *** electrokynetic injection, DL – detection limit.*

Table 7. CE determination conditions and detection limits for benzoate.

Detection mode	Buffer	pH	Additives	DLt, M	Ref.
I. Photometric					
1.1 Direct					
200 nm	tetraborate,100 mM/ boric acid, 400 mM	8,5-9,3		$1{,}47\times10^{-6}$ $3{,}8\times10^{-10}$ **	[83]
210 nm	phosphate, 50 mM	8	0,001 % HDB, 25 % 2-propanol	$6{,}6\times10^{-7}$	[62]
214 nm	acetate, 25mM/TRIS	4,2	1 mM Ni(II)[a]		[61]
	MES/TRIS, 50 mM	5,5	1 mM Ni(II)[a]		[61]
225 nm	phosphate, 1 mM	4			[84, 85]
1.2 Indirect					
210 nm	phtalate, 5 mM	7	0,25 mM CTAB		[54]
	1,2-dimethylimidazole, 4mM/ trimellitate, 1,0 mM	7	*	8×10^{-7}	[6]
254 nm	chromate, 5 mM	8	OFM[a]		[27]
264 nm	4-aminobenzoate, 7,5 mM	9,6	55 µM TTAH, 0,76 Ba(II)		[16]
280 nm	NDC, 2 mM	8-11	0,5 mM TTAB	1×10^{-6}	[50]
II. Electrochemical					
Conductometric	tetraborate, 2 mM	9,2	0,02 mM Ba(II)		[36]
III. Mass spectrometry					
	acetate, 20 mM	8,5			[44]

*a – commercial products, b – pretreated column, * coelectrosmotic mode, ** with stucking, *** electrokynetic injection, DL – detection limit.*

Table 8. CE determination conditions and detection limits for phtalate.

Detection mode	Buffer	pH	Additives	DL, M	Ref.
Photometric					
1. Direct					
185 nm	tetraborate, 25 mM	9-10	0,5 mM TTAB, 2,25 mM Ba(II), 2 mM β-cyclodextrin,		[59]
210 nm	phosphate, 50 mM	8,0	0,001 % HDB, 25 % 2-propanol	$4{,}2\times10^{-7}$	[62]
214 nm	acetate, 25mM/TRIS	4,2	1 mM Ni(II)[b]		[61]
	MES/TRIS, 50 mM	5,5	1 mM Ni(II)[b]		[61]
2 Indirect					
250 nm	pyromellitic acid, 2,5 mM	7,7	0,75 mM HMH, 1,6 mM triethanolamine		[48]
254 nm	chromate, 5 mM	8,0	OFM[a]		[81]
	PDC, 9 mM	7,8	0,5 mM TTAB	$3{,}6\times10^{-6}$	[55]
264 nm	4-aminobenzoate, 7,5 mM	9,6	55 μM TTAH, 0,76 Ba(II)		[16]
280 nm	NDC, 2 mM	8-11	0,5 mM TTAB	1×10^{-6}	[50]
314 nm	indigo-tetrasulfonate, 500 mM/ BIS-TRIS, 2,67 mM	6,8	*	2×10^{-7}	[67]

*a – commercial products, b – pretreated column, * coelectrosmotic mode, ** with stucking, *** electrokynetic injection, DL – detection limit.*

List of abbreviation:

EOF modifiers:

CPB – cetylpyridinium bromide

CTAB – cetyltrimethylammonium bromide

CTAH – cetyltrimethylammonium hydroxide

DETA – bis-(2-aminoethyl)-amine (diethylenetriamine)

DoTAH – dodecyltrimethylammonium hydroxide

HDB – 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide

HMH – hexamethonium hydroxide

MTAB – myristiltrimethylammonium bromide

PVA – polyvinyl alcohol

p-AB – 4-aminobenzoic acid

TTAB – tetradecyltrimethylammonium bromide

OFM – organic flow modifier

Buffers:

BIS-TRIS – 1,3-bis[tris(hydroxymethyl)amino]propane

CHES – 2-(N-cyclohexylamino)ethanesulfonic acid

HEPES – N-(2-hydroxyethyl)piperazine-N'-2-ethane sulphonic acid

HIS – histidine

MES – 2-(N-morphlino)ethanesulfonic acid

NDC – 2,6-Naphthalenedicarboxylic acid

NDS – Naphtalenedisulfonate

NTS – Naphtalenetrisulfonate

Nitroso-R salt - 1-nitroso-2-naphtol-3,6-disulphonic acid

126NNS – 1-nitroso-2-naphtol-6-sulphonic acid

216NNS – 2-nitroso-1-naphtol-6-sulphonic acid

PDC – 2,6-Pyridinedicarboxylic acid

PyDC – 2,3-pyrazinedicarboxylic acid

TRIS – tris(hydroxymethyl)aminoethane

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