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Development of a solid-phase extraction and derivatization method for polar carboxylic acids from aqueous extracts of inorganic multi-component incineration residues

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Abstract A rapid and reliable GC/MS (EI and CI) method was developed for the identification of short-chain mono- and dicarboxylic acids in complex and strongly alkaline residues of municipal waste incineration. Such residues contain organic carboxylic acids in the mg/kg to µg/kg range, which may contribute to the mobilization of heavy metals. However, the alkalinity and the high salt loads of the matrix were found to be a serious problem in the analysis of short chain acids. Extraction with water, solid phase extraction, and derivatization were studied under these conditions. Solid-phase extraction with polymeric sorbents and derivatization with diazomethane can be combined in a reproducible manner to yield a robust and simple method which can be applied for screening unknown solids due to its wide applicability and the well identifiable methyl esters. Absolute recovery rates varied between 20 and 85% depending on the individual acids.

1 Introduction

Short-chain carboxylic acids and dicarboxylic acids in aqueous solutions can be determined in medicine and food chemistry [1–3] by a great variety of methods [4–6]. In strongly saline, alkaline residues arising from the incineration of, e.g., municipal and industrial waste, the total content [7] of organic compounds or special, non-polar fractions of acute toxicity [8–10] are analyzed.

Residues from waste incineration plants among others consist of silicates, metals, metal oxides, and inorganic salts. Low-molecular organic components represent direct products of low-temperature carbonization during incomplete incineration or are generated by microbial decomposition of macromolecular residual components during storage or disposal [11]. Carboxylic acids may affect the

storage stability of these residues by reducing the pH value and increasing the mobility of heavy metals. To evaluate the long-term stability of slag depositions, the inventory of short-chain acids, therefore, has to be determined.

For detection of polar organic acids in such a matrix, the slags have to be extracted with water and not with organic solvents [12]. The aqueous extracts contain mainly chlorides and sulfates in the g/L range. This causes problems in the processing and isolation of strongly polar acids. It was the objective of the present work to develop a method which allows qualitative and quantitative determination of a large number of mono- and dicarboxylic acids in aqueous extracts of incineration residues. GC/MS with chemical ionization (CI) was used in addition to electronical ionization, to obtain information on the molecular weight of possibly unknown compounds [13, 14].

By derivatization of the polar acid group, the chromatographic properties of carboxylic acids can be improved significantly [1, 15].

Derivatization directly in an aqueous solution with e.g. pentafluorophenyldiazoethane (PFPDE) [16], pentafluorobenzylbromide (PFB-Br) [17] or pyrenyldiazomethane (PDAM) [18] would have the advantage of the isolation of acids from the extracts being strongly facilitated or even superfluous [19]. The by-products [20] generated by the above reactants, low volatility of dicarboxylic acids derivatives and the residues of the derivatization reactants [17], however, cause significant problems.

Using silylation reactants, high yields can be obtained for the derivatization of carboxylic acids to highly volatile silyl esters [21]. Furthermore, some silylation agents can be used to derivatize hydroxy groups, also [22].

Conversion of the carboxylic acids into their methyl esters is most frequently applied for the derivatization of carboxylic acids [23, 24]. Therefore a large number of reference spectra of methyl esters are available from commercial mass spectra libraries. Known methods [23] for preparation of methyl esters cannot simply be transferred to our case with complex impurities. Therefore, comparative investigations with various methylating reactants were performed.

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Due to the hydrolytic sensitivity of the respective reactants, methylations and silylations of carboxylic acids cannot be carried out directly in water. Prior to derivatization, separation and clean-up are necessary.

To separate polar carboxylic acids from an aqueous solution, liquid-liquid extraction (LLE) [25], solid-phase extraction (SPE) [26, 27], and solid-phase microextraction (SPME) [19, 28] are commonly applied. Recovery rates are generally rather low due to the high polarity of these substances and the resulting separation problems. Protonation of organic acids enhances their lipophilic properties considerably, which generally serves as a starting point of separation from inorganic anions. In our case, ion pairing reactants [17] were not suitable because of the high salt load in the extracts. The advantages of solid-phase extraction as compared to liquid-liquid extraction include shorter analysis times, less, more reproducible handling and only little use of solvents [26, 29]. For very polar dicarboxylic acids in particular, SPME seemed to be unsuitable, although this simple and rapid method already proved to be applicable for short-chain monocarboxylic acids [19].

SPE has already been applied for the isolation of rather lipophilic phenoxycarboxylic acids and long-chain fatty acids [30, 31]. Our study focused on the development of a reversed-phase solid-phase extraction with a styrene-divinylbenzene copolymer to extract polar carboxylic acids from aqueous extracts. Due to the high salt load of the samples, ion exchange or diol phases cannot be applied. Conventional silica-based reversed phases (C_8 or C_{18}) are subject to hydrolysis at pH values below 2. After SPE the carboxylic acids may be eluted with any suitable organic solvent and subjected to derivatization and GC/MS analysis. Applicability of the method developed is demonstrated using extracts of doped slags.

2 Experimental

2.1 Chemicals. All chemicals used were at least analytical grade (> 99% purity). Carboxylic acids for standards were obtained from Merck, Darmstadt and Aldrich, Steinheim. Methyl ester standard substances were purchased from Aldrich, Steinheim. Methylating reagents MSTFA (N-methyl-N-(trimethylsilyl)-trifluoroacetamide, 0.2 M in diethyl ether), TMSH (trimethyl-sulfonium-hydroxide, 0.2 M in methanol) were available from WGA, Düsseldorf. Diazomethane (DAM) was freshly prepared from Diazald (Aldrich) and was stable for at least one week at -80°C [32]. Note: Diazomethane is highly toxic, carcinogenic and explosive. Synthesis, storage, and application in hoods with explosion screen and protective clothing only. All solvents were of LiChrosolv® or Suprasolv® quality and supplied by Merck, Darmstadt. The eluent was water from a milli-Q-plus facility. The drying agents Na_2SO_4 , CaCl_2 and molecular sieve 3 Å of Merck were subjected to additional drying in an oven at 200°C for two days.

The solid phases were purchased as pre-packed columns (200 mg material) from J.T. Baker, Gross-Gerau (SDB-1-material). As an alternative, loose HR-P material was purchased from Macherey-Nagel, Düren, and filled into glass columns. No significant differences were observed between both materials.

2.2 Preparation of solid standards. Slags from a municipal waste incineration plant were dried for 2 h at 105°C , ground (< 200 µgm) and subjected to annealing in air at 550°C for a week in order to

oxidize all organic constituents. By means of X-ray diffraction, it was ensured that annealing had not caused any mineralogical conversions. These slags were then doped with 1 mL aqueous acid mixture. Acid concentration in the slag was 100–200 µg/kg. For doping, acid droplets were added with a calibrated pipette. Subsequently, the mixture was homogenized thoroughly in the mortar. Prior to extraction, the doped samples were stored for one day at room temperature. Samples that had been stored for a longer period of time (up to 3 months) yielded the same recovery rates.

2.3 Extractions. The slags were extracted by means of a hot extraction system developed at our institute [33, 34] in analogy to the extractors offered by Perstorp Analytical Company, Rodgau (Soxtec®). Glass-fiber extraction thimbles from Schleicher & Schüll, Dassel were subjected to annealing in air at 550°C one week prior to use with a view to remove organic impurities.

2.4 Solid-phase extraction. Solid-phase extraction was performed using a Baker SPE-12 unit with a Baker vacuum chamber, column adapters and Teflon® flow valves. Enrichment was carried out in accordance with the following instructions: The SPE columns were subjected to conditioning with 3×1 mL methanol, followed by 3×1 mL water (pH 1, NaCl-saturated). 5 mL of the sample (about 1 mg/L per acid, < pH 1, NaCl-saturated) were added slowly (1 mL/min). After the addition of the sample, the residual water was removed from the columns in a centrifuge at about 1000 rpm for 10 min and the columns were then dried in a stream of nitrogen for 1 min. For elution, a Na_2SO_4 column was connected to the outlet of the SPE column by column adapters (arrangement see Fig. 1). Then, slow elution with 4×1 mL MTBE (methyl-tert-butyl-ether) followed. The eluate was collected in pre-calibrated 5 mL V-shaped glasses (Bender & Hobein, Bruchsal). The collected eluates were reduced to about 1 mL in a nitrogen flow and subjected to derivatization. This procedure allowed rapid processing without additional clean-up operations being required.

2.5 Derivatizations. For derivatization, DAM, MSTFA, TMSH and $\text{MeOH}/\text{H}_2\text{SO}_4$ were investigated. MTBE standard solutions with an analytical agent content of 1–20 mg/L and the corresponding concentrations (cf. Table 1) of acid, water, or salt were produced to evaluate the influence of impurities on derivatization. Then, 0.2 M DAM, TMSH, or MSTFA solutions were added to 1 mL of the above solutions and subjected to reaction in closed vials under the above conditions. When using DAM and MSTFA, the excessive reactant was removed in a gentle stream of nitrogen. TMSH is decomposed into highly volatile products in the injector. Derivatization with TMSH partly takes place in the injector. In the $\text{MeOH}/\text{H}_2\text{SO}_4$ tests concentrated sulfuric acid was added to 1 mL methanolic standard in a 10 mL measuring flask giving a 5:1 or

Fig. 1 Arrangement used for the elution of the analytical agents following solid-phase extraction. (a) syringe, (b) SPE-column, (c) Na_2SO_4 -column for drying, (d) graduated and calibrated collection vial

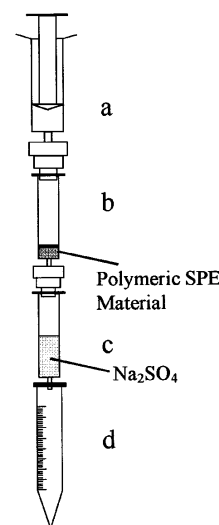


Table 1 Survey of the derivatization parameters investigated. In addition to the parameters given, mixed standards were produced with H₂O, H₂SO₄, and salt to examine possible cross-effects

Reagent	DAM (0.2 M)	TMSH (0.2 M)	MSTFA (0.2 M)	MeOH/H ₂ SO ₄
Amount	100/200/400/800 μ L	100/250/400/800 μ L	100/200/400 μ L	1:5/1:10
Temperature	-70 °C/+4 °C/RT	50 °C	50 °C	50 °C
Time	30 min/1 h/2 h	15 min/1 h/2 h	10 min/1 h	30 min/1 h/2 h
H ₂ SO ₄	100/200 mg/L	100/200 mg/L	100/200 mg/L	—
H ₂ O	500/2000/5000/10 000 mg/L	1000/2000/5000/10 000 mg/L	1 000/2000/5000/10 000 mg/L	500/1000/4000 mg/L
Salt ^a	NaCl/Na ₂ SO ₄ /NaHCO ₃	NaCl/Na ₂ SO ₄ /NaHCO ₃	NaCl/Na ₂ SO ₄ /NaHCO ₃	NaCl/Na ₂ SO ₄

^a 100 mg/ml of each salt was added

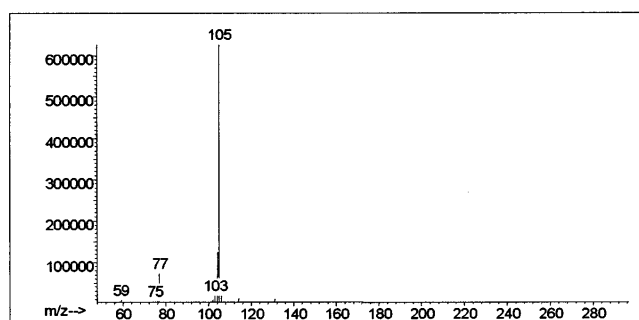
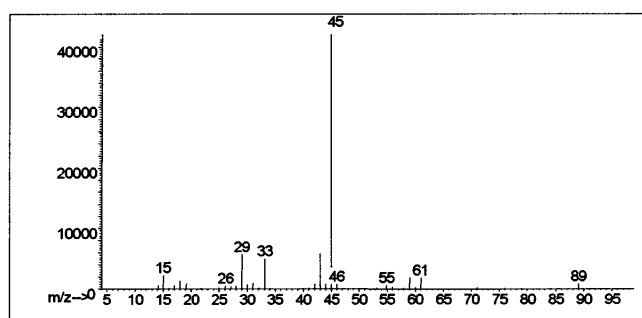


Fig. 2 *Top*: EI spectrum of methyl lactate. The molecular mass of 104 is not visible. *Bottom*: By the molecule-ion impact with methanol, the M+1 peak of methyl lactate becomes the base peak

10:1 excess of methanol. After the reaction time, the solution was filled up with a saturated NaCl solution, neutralized by addition of NaHCO₃, and extracted with 5 \times 1 mL MTBE. The extracts were evaporated to 1 mL and analyzed.

2.6 GC/MS analyses. GC/MS analyses were performed using the Saturn 2000 system of Varian, Darmstadt. This system consists of an autosampler 8200, a split/splitless injector 1078 (back-pressure controlled), and an ion-trap detector. Methanol served as the reactant gas for CI. Via a special connection, it could be used as a liquid. Chromatographic separation was carried out with a fused-silica capillary column (Hewlett-Packard, HP-1, 60 m, 0.25 mm ID, 0.25 μ m film thickness). Analysis was run at the following temperatures: injector: 270 °C constant; furnace: 45 °C for 6 min, 4 °C/min up to 250 °C, 10 °C/min up to 280 °C, 280 °C for 10 min; transfer line: 250 °C; ion trap: 150 °C. Carrier gas was helium 6.0, with a flow of about 1 mL/min and 16 psi (110 kPa) head pressure. Splitless injection of 2 μ L samples was used. The change from EI to CI was software controlled, which allowed the analysis of a sample first in the EI and then in the CI mode. For CI analysis of methyl carboxylates, a method was developed, which mainly leads to the detection of M+1 peaks (cf. Fig. 2). Quantification of the results was based on peak areas from RIC (reconstructed ion chromatogram) and single ion chromatograms.

2.7 Calibration. The related acids were selected to cover a wide range of polarity. To determine the actual recovery rate in all steps, external standards were used. In all critical steps, detection strongly depends on the specific properties of the individual acids. Hence, several internal standards would have to be applied, which may cause disturbing coelutions in real samples. Methyl ester solutions in MTBE were prepared in concentrations of 0.1 mg/L to 100 mg/L. At least 4-point calibrations were run over a range of two orders of magnitude. Typically, analysis was performed alternating injection of two samples and two standard solutions each.

3 Results and discussion

3.1 Derivatizations

Usually, esterification in low concentrations of mono- and dicarboxylic acids is not completely quantitative even with strong methylation reactants. The degree of conversion does not only depend on the type of carboxylic acid (degree of dissociation, polarity), but also on the type of solvent. When using the eluates of solid-phase extraction, it cannot be ensured that they are free of water, acid, or salt in spite of the downstream Na₂SO₄ column. Derivatizations with DAM, TMSH, MSTFA, and MeOH/H₂SO₄ were investigated to check the influence of impurities on derivatization.

At the same time, the effect of the derivatization duration and temperature as well as of the reactant volume added were investigated. Table 1 gives a survey of the parameters studied. In addition, standard solutions were produced for each reactant. They contained moderate concentrations of all impurity components to study possible cross-effects.

3.1.1 Derivatizations with MeOH/H₂SO₄

The best results were obtained using the following approach: 1 mL methanolic solution of the analytical agent is filled into a 10 mL measuring flask. After addition of 100 μ L concentrated H₂SO₄, the flask is closed and derivatization takes place at 50 °C for a period of 2 h. Derivatization rates were hardly affected by salt and water. However, only small yields of lactic acid, oxalic acid, malic acid, and salicylic acid could be detected. A major drawback of this derivatization method is the low efficiency of extraction with MTBE, the high thermal stress

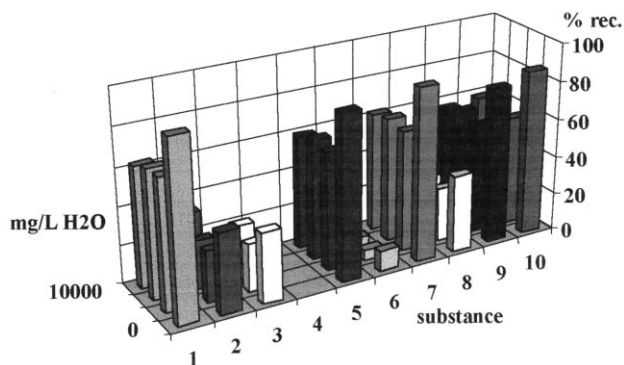


Fig.3 Recovery rates with TMSH at increasing water contents. Poor recovery rates were achieved for strongly polar acids such as oxalic acid, malonic acid, and malic acid. (Succinic acid coeluted with by-product and was not quantified.) For assignments of substances cf. Table 2

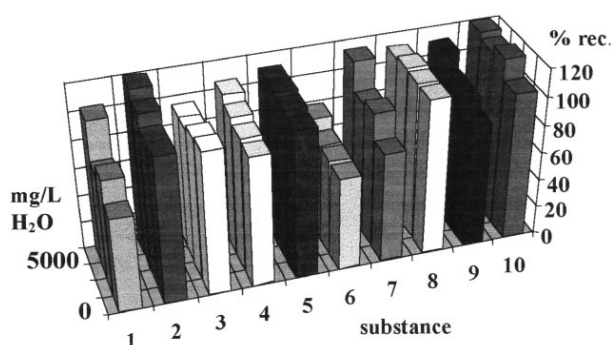


Fig.4 Recovery rate with DAM with increasing water content. A content of about 5000 mg/L water even yields slightly improved recovery rates for most acids. For assignments of substances cf. Table 2

on the samples during reaction with concentrated H_2SO_4 , and the relatively long time needed.

3.1.2 Derivatization with TMSH

The best conversion rates were achieved with 200 μ L reactant at a reaction time of 1 h (cf. Fig. 3). Flash derivatization with derivatization taking place only in the hot injector did not prove to yield stable results with short chain acids. Water, salt, and acid had a significant negative influence on the recovery rate. In the impurified samples, the content of disturbing by-products increased significantly. These by-products are supposed to be hydrolytic products of the derivatization reactant and coeluted with succinic acid, disturbing quantitation. Noteworthy is the occurrence of methyl dimethyl malonate which is probably generated by the protonation of the H-acid function of dimethyl malonate. TMSH is hardly suitable for use in humid or salt-containing samples.

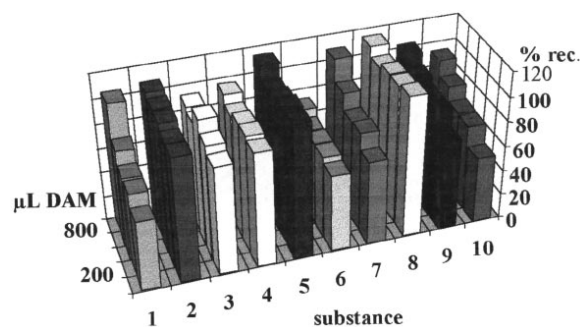


Fig.5 Derivatization yield as a function of DAM addition. At about 400 μ L DAM, side reactions start to increase considerably. For assignments of substances cf. Table 2

3.1.3 Derivatization with MSTFA

Good conversion rates were achieved with MSTFA in clean samples. A reactant volume of 200 μ L and a reaction time of 1 h proved to be optimum. However, already small concentrations of water or acid caused very unstable, unreproducible recovery rates. Moreover, concentration of disturbing by-products (siloxanes) increased significantly when water was added. Also chromatographic columns were strongly affected by MSTFA samples. MSTFA did not seem to be suitable for the derivatization conditions investigated.

3.1.4 Derivatization with DAM

Homogeneous recovery rates were achieved with diazomethane even in the presence of impurities. The best results were obtained by an addition of 500 μ L DAM solution (cf. Fig.5) at dry ice temperature and a reaction time of 2 h at 4 °C. The recovery rates are represented in Fig.4 as a function of increasing water content. Although the recovery rate of some acids (butyric acid, octanedioic acid) can be increased by higher DAM volumes, the optimum yield and by-product formation seems to be reached at 500 μ L. When adding 800 μ L DAM, several disturbing side reactions took place, such as excessive formation of products from hydrolysis and polymerization. Maleic acid could not be esterified with diazomethane. Probably, the double bond is opened to yield very short chain acids. The reaction products of maleic acid could not be quantified due to their volatility. Production and storage of DAM at dry ice temperature did not cause any problems.

3.2 Solid-phase extraction

Separation of polar carboxylic acids from inorganic anions such as chloride and sulfate on reversed-phase materials is feasible in strongly acidic solutions. The decisive advantage of this method is the robustness against inorganic impurities and the simple, reproducible procedure without additional organic reactants being needed. It was

Table 2 Recovery rates (REC) and relative standard deviations (STD) of derivatizations with diazomethane at 500 mL DAM, 1000 µg/mL H₂O, addition of salt. (Number of measurements: 9, ME = methyl ester, DME = dimethyl ester)

No.	Substance	REC (%)	STD (%)
1	Butanoic acid, ME	59	2
2	Lactic acid, ME	98	2
3	Oxalic acid, DME	92	2
4	Butanedioic acid, DME	123	5
5	Benzoic acid, ME	109	1
6	Malic acid, DME	59	4
7	Octanoic acid, ME	73	3
8	Salicylic acid, ME	112	1
9	Hexanedioic acid, DME	79	2
10	Octanedioic acid, DME	88	2

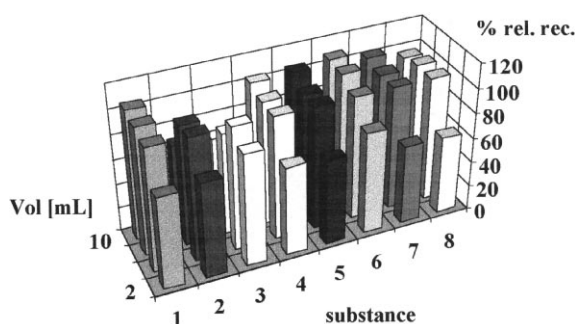


Fig. 6 Recovery rate as a function of the sample volume applied. At a sample volume of 10 mL, significant self-elution of the highly water-soluble acids is observed. With 2 mL volume, sample application was ineffective. For assignments of substances cf. Table 3

investigated, for the first time how these very polar carboxylic acids may be enriched by solid phase extraction with polymer based adsorbents.

For determining recovery rates, standards were produced in an NaCl- and Na₂SO₄-saturated solution. The concentration was about 1 mg/L per acid. The acids were selected to cover a wide range of polarity. Furthermore, the especially critical acids, i.e. lactic acid, oxalic acid, salicylic acid, and citric acid were to be included.

Investigation of the SPE procedure showed that the volume of the eluting solvent (3–6 mL MTBE) and the exact volume of the sample (3–6 mL) were uncritical in the given ranges. At higher sample volumes (10 mL), however, self-elution of the analytical agents was observed (cf. Fig. 6). The optimum sample feeding rate turned out to be about 1 mL/min. In addition, the pH of the sample must be at or below 1. The columns have to be dried in a nitrogen flow for a short time only, as losses may occur in the relatively highly-volatile acids e.g. butyric acid. The recovery rates obtained by 9 measurements with the optimized procedure are summarized in Table 3. The low recovery rates above all for lactic acid and malonic acid result from their high polarity. With the described method, reproducible results can still be obtained. Oxalic acid and citric acid could not be detected in a stable manner by this

Table 3 Recovery rates (REC) and relative standard deviations (STD) of derivatization and solid-phase enrichment. (Number of measurements: 9, ME = methyl ester, DME = dimethyl ester)

No.	Substance	REC (%)	STD (%)
1	Butanoic acid, ME	51	5
2	Lactic acid, ME	42	6
3	Propanedioic acid, DME	65	7
4	Butanedioic acid, DME	84	5
5	Benzoic acid, ME	72	9
6	Salicylic acid, ME	80	5
7	Hexanedioic acid, DME	67	9
8	Octanedioic acid, DME	52	11

method, as they were not sufficiently lipophilic even at pH 0.5. Quantification of octanedioic acid was unprecise, as ubiquitous dimethyl phthalate (e.g. from GC septums) coeluted even under varying gas chromatographic conditions and affected quantitation masses. All other acids could be separated and detected reliably.

3.3 Extraction

It was the objective to demonstrate that organic acids can be extracted with water from a target matrix containing a number of inorganic anions and cations as well as silicates, elementary metals (iron, aluminium) and elementary carbon. Possible problems were supposed to arise from formation of heavy metal complexes, irreversible bonding of acids to silicates by sorption, reactions with catalytic metals, and the relatively high thermal load during extraction with water.

All extracts were produced under identical conditions: 50 g solid standard (100–200 µg/kg per acid) were filled into extraction thimbles, subjected to extraction in boiling water for 3 h and backwashed overnight using the condensate. The thus obtained eluates were evaporated to about 5 mL, acidified to pH 1 with sulfuric acid and subjected to the solid-phase extraction described. The RIC chromatogram of an extract is shown in Fig. 7. Retention times and recovery rates of the individual acids are evident from Table 4.

The extraction step results in increased values of dimethyl phthalate and alkanes in blanks. Vial caps, septums and seals that are required for tightening the extraction vessels were found to be possible sources.

Lactic acid and salicylic acid are detected with poor yields. However, they can be determined in a semi-quantitative manner at least. The reduced recovery rate of these acids may be attributed to both thermal decomposition and losses by sorptions and complex formation. Extraction of most carboxylic acids is rather efficient and no detrimental matrix-effects on the recovery rates were observed. For a reliable detection and quantification, minimum concentrations are 50 µg/kg for most acids. Lactic acid and salicylic acid may be quantified as of 100 µg/kg only. The detection limits are not determined by the ana-

Fig. 7 RIC (reconstructed ion chromatogram) of a solid standard extract per acid about 200 µg/kg. For assignment of the individual peaks: cf. Table 4

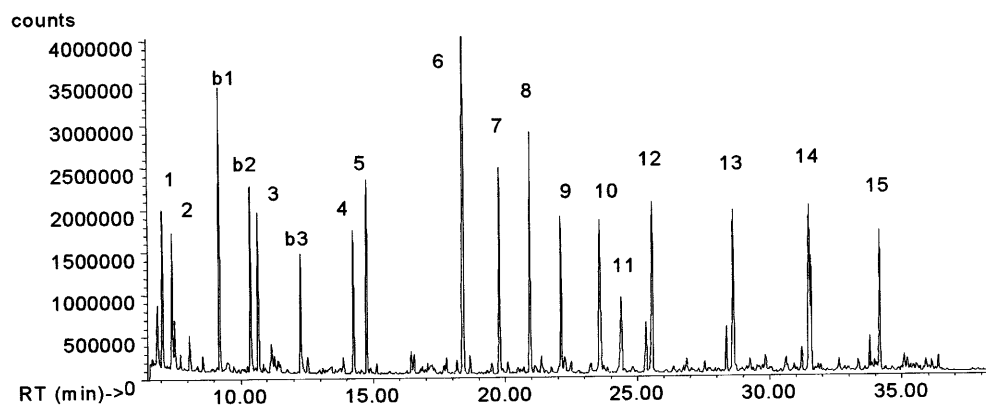


Table 4 Retention times and recovery rates (REC) of organic mono- and dicarboxylic acids from slag extracts. (Number of measurements: 14, ME = methyl ester, DME = dimethyl ester) (Chromatogram, see Fig. 7)

No.	RT (min)	Substance	Conc. (µg/kg)	REC (%)	STD (%)
1	7.48	Butanoic acid, ME	188	48	2
2	8.51	Lactic acid, ME	212	28	10
b1	9.02	Blank (Derivatization)			
b2	9.76	Blank (Derivatization)			
3	11.41	Pentanoic acid, ME	196	73	7
4	15.51	Propanedioic acid, DME	224	36	15
5	16.13	Hexanoic acid, ME	184	54	3
b3	20.15	Blank (MTBE-Peroxide)			
6	20.46	Butanedioic acid, DME	252	85	13
7	22.12	Methyl-butanedioic acid, DME	200	47	2
8	23.49	Benzoic acid, ME	196	62	3
9	24.94	Pentanedioic acid, DME	192	49	8
10	26.72	Phenylacetic acid, ME	196	53	3
11	27.67	Salicylic acid, ME	206	20	28
12	29.16	Hexanedioic acid, DME	202	57	6
13	32.93	Heptanedioic acid, DME	216	55	6
14	36.48	Octanedioic acid, DME (+Phthalate)	195	51	14
15	39.79	Nonanedioic acid, DME	206	47	8

lytical process itself, but rather by the background of the chromatogram.

4 Conclusions

The method described allows the simple and rapid detection of a large number of polar, organic carboxylic acids and dicarboxylic acids in alkaline residues. It was shown, that by using SPE with polymer-based solid phases, efficient extraction of even highly polar carboxylic acids and dicarboxylic acids from aqueous solutions with considerable salt loads is achieved in a short time. Acids with very high pKa values, such as oxalic acid and citric acid, however, may not be enriched.

Methylation by diazomethane is well suited for the derivatization of short-chain carboxylic acids. In the studies performed, diazomethane turned out to yield the most reproducible results in the presence of impurities like water, acid or salts and is hence preferred to comparable reactants.

A drawback is the high volatility of the generated methyl esters, which does not allow the detection of

C₁–C₃ monocarboxylic acids. However, a large number of dicarboxylic acids may be separated well and with high resolution. The main advantages of GC/MS coupling are the high resolution and the good identification of unknown compounds by chromatography. The use of chemical ionization as an additional means for the identification brings about a number of advantages as compared to pure EI, in particular for the easily fragmenting carboxylates.

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