ELSEVIER

Journal of Chromatography A, 898 (2000) 111–124

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Analysis of polycyclic aromatic hydrocarbons, phenols and aromatic amines in particulate phase cigarette smoke using simultaneous distillation and extraction as a sole sample clean-up step

J.B. Forehand, G.L. Dooly, S.C. Moldoveanu*

Brown & Williamson Tobacco Corp., Research & Development, 2600 Weaver Road, Macon, GA 31217, USA

Received 25 April 2000; received in revised form 31 July 2000; accepted 2 August 2000

Abstract

Polycyclic aromatic hydrocarbons (PAHs), phenols and aromatic amines can be analyzed in particulate phase mainstream cigarette smoke using simultaneous distillation and extraction (SDE) as a unique sample clean-up step. All analytes are determined from the same smoke sample using GC–MS. The smoke from 20 cigarettes is collected on a Cambridge smoke pad where a mixture of internal standards is added. The Cambridge smoke pad is extracted in a SDE apparatus using water–CH_2Cl_2. The SDE extract is analyzed directly for PAHs, for phenols after silylation, and for amines after derivatization with heptafluorobutyric anhydride. Excellent results in agreement with data reported in the literature are obtained by this procedure.

Keywords: Cigarette smoke; Simultaneous distillation and extraction; Polynuclear aromatic hydrocarbons; Phenols; Aromatic amines

1. Introduction

Cigarette smoke analysis for specific compounds such as polynuclear aromatic hydrocarbons (PAHs), phenols, and aromatic amines is the subject of numerous studies. Each group of compounds can be analyzed by a variety of procedures that commonly involve a sample preparation step. This sample preparation step is required because smoke is a very complex mixture, and the analytes of interest are at trace levels [1]. Commonly, after smoking the cigarettes and collecting the particulate phase on a smoke pad (Cambridge pad), the particulate phase is extracted and processed [2]. Concentration of the analytes and elimination of a significant portion of undesired components from the smoke matrix is achieved by clean-up procedures that are usually different for each group of analytes. In PAHs analysis, for example, typical clean-up procedures are based on multi-step separations [3–10] using solid-phase extractions (SPEs), or small-scale preparative chromatography. Phenols are analyzed in smoke either after a clean-up step [11–17] using solvent extraction, SPE, etc., or using trimethylsilylation of

*Corresponding author. Tel.: +1-912-464-3419; fax: +1-912-464-4017.

E-mail address: smoldov@aol.com (S.C. Moldoveanu).

0021-9673/00/$ – see front matter
PII: S0021-9673(00)00827-X

the smoke pad extract [18]. Amines are also analyzed in smoke usually requiring two clean-up steps followed by derivatization [19–27]. The clean-up steps for amines may apply the amine extraction from the sample using diluted solutions of a strong acid in water, followed by a pH change, and reextraction of amines in an organic phase. Further clean-up steps using SPE are also used in certain applications.

The present paper describes a procedure that allows successful analysis of PAHs, phenols, and aromatic amines using simultaneous (steam) distillation and extraction (SDE) as a sole clean-up step and using one single smoke sample for all analytes. SDE is a well known technique used for selective separation of certain fractions from complex samples [28–31]. The technique was first used by Likens and Nickerson [28] and later applied for the analysis of essential oils [29]. Various descriptions of a SDE apparatus are available [29] and the technique is common. It has been used more frequently for the analysis of volatiles [30], but by extending the extraction time, good results can be obtained even for compounds as heavy as dibenzanthracene [31].

For the analysis of particulate phase smoke, SDE offers a significant reduction in the effort required for performing the analysis. This is due in part to the simplicity in sample preparation. Also, the capability to perform multiple analyses using one smoke collection and a sole clean-up step is a significant advantage of the procedure.

2. Experimental

The particulate phase from 20 cigarettes is collected using a Borgwaldt RM 20/CS smoking machine with a 92 mm smoke pad. Smoking can be performed under any specific protocols such as those recommended by US Federal Trade Commission (FTC) [32], International Standard Organization (ISO) [33–35], or other [36]. For some smoking regimes such as Massachusetts recommended conditions [34], 10 cigarettes are sufficient. After smoke collection the total particulate matter (TPM) accumulated on the pad is weighed.

2.1. Sample preparation using SDE

After weighing the smoke pad to determine the TPM, a solution in isopropanol containing the internal standards listed in Table 1 is added to it. The spiked smoke pad, 250 ml water and 30 g sodium chloride are placed in the sample flask of the SDE apparatus (microsteam distillation apparatus, part 8910, Alltech). The solvent flask contains 15 ml CH_2Cl_2. This apparatus is shown in Fig. 1. The two flasks are boiled for 5 h with efficient cooling of the condenser. The temperature of the cooling fluid was maintained around 0°C and all the vapors are properly condensed in the system. The optimum extraction time was established by interrupting the process for different samples at 3, 4 or 5 h, respectively. Each sample was re-extracted for an extra 2 h. No compounds were detected in the organic phase for the re-extract of the sample that initially was processed for 5 h, while the other samples still had traces of extractable components. Although a relatively long time is needed for extraction, this disadvantage is circumvented by operating ten SDE

Table 1
Internal standards used in smoke analysis with SDE sample preparation

Compound	Formula	Amount used
PAHs		
[$^2H_8$]-Naphthalene	$C^2_{10}H_8$	7 μg
[$^2H_{10}$]-Fluorene	$C^2_{13}H_{10}$	4 μg
[$^2H_{10}$]-Anthracene	$C^2_{14}H_{10}$	1 μg
[$^2H_{10}$]-Pyrene	$C^2_{16}H_{10}$	500 ng
[$^2H_{12}$]-Chrysene	$C^2_{18}H_{12}$	500 ng
[$^2H_{12}$]-Benzo[*a*]pyrene	$C^2_{20}H_{12}$	500 ng
[$^2H_{14}$]-Dibenz[*a*,*h*]anthracene	$C^2_{22}H_{14}$	500 ng
Phenols		
[$^2H_6$]-Phenol	$C^2_6H_6O$	120 μg
[$^2H_8$]-*o*-Cresol	$C^2_7H_8O$	50 μg
[$^2H_6$]-Hydroquinone	$C^2_6H_6O_2$	640 μg
Aromatic amines		
[$^2H_5$]-Aniline	$C^2_6H_5NH_2$	4 μg
[$^2H_7$]-*o*-Toluidine	$C^2_7H_7NH_2$	1 μg
[$^2H_7$]-2-Naphthylamine	$C^2_{10}H_7NH_2$	500 ng
[$^2H_9$]-4-Aminobiphenyl	$C^2_{12}H_9NH_2$	500 ng
[$^2H_8$]-Benzidine	$C^2_{12}H_8N_2H_4$	500 ng

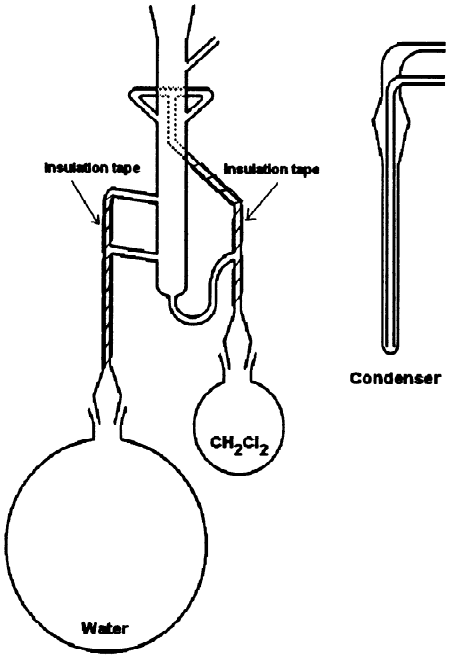

Fig. 1. Steam distillation and extraction apparatus.

systems in parallel, which allows simultaneous processing of 10 samples.

2.2. Experimental conditions for PAH determination

For the analysis of PAHs, 1 ml of the CH_2Cl_2 SDE extract was concentrated to approximately 100 μl and 1 μl was injected into the GC–MS system without further treatment. A Hewlett-Packard 6890 GC system interfaced to a Hewlett-Packard 5973 mass spectrometer was used for the analyses. The GC system was equipped with an SGE BPX5 column (30 m×0.25 mm I.D., 0.25 μm film thickness). The injection temperature was 280°C, initial oven temperature 45°C, initial hold time 5.0 min, rate of temperature program 10°C/min, final oven temperature 310°C, final hold time 5 min. The carrier gas was helium. A pulse splitless injection of 1 μl was used, with pulse pressure 30 p.s.i. (1 p.s.i.= 6894.76 Pa), constant flow of 2 ml/min, starting column head pressure 16.5 p.s.i., split valve flow 50 ml/min and purge valve on time 1.0 min. The MS operated in positive electron ionization (EI+) with selected ion monitoring (SIM) mode. Typical EI+ mass spectra of PAHs show little fragmentation. This lack of fragmentation in the spectrum is a disadvantage regarding the presence of confirming ions for the identification of PAHs, but it is an advantage regarding the sensitivity when using SIM detection. SIM mass spectral data for molecular ions of each of the PAHs analyzed were collected in 10 time groups from 7 to 27 min. All measurements for PAHs were done using their molecular ions. The SIM chromatogram for a solution of 0.5 μg/ml standards and deuterated standards of PAHs is given in Fig. 2. Benzo[*b*]fluoranthene and benzo[*k*]fluoranthene are not separated (peak 14) and also, dibenz[*a*,*h*]anthracene and dibenz[*a*,*c*]anthracene elute in the same peak (peak 19).

The SIM ion group data are converted into extracted ion chromatograms for each particular compound (ion), and the areas under each peak are determined for further quantitation. The quantitation is done based on the ratio of peak areas of the analytes and corresponding internal standards. For this purpose, response factors (RFs) for each compound (relative to the internal standards) are initially obtained. The response factors are calculated by dividing the areas of the chromatographic peaks for standards of the analytes by the areas of corresponding deuterated internal standards, at equal concentrations. The RFs for each compound are obtained by averaging the RFs calculated from three runs using the formula:

$$\mathrm{RF} = (\mathrm{AREA}_{\mathrm{analyte}}/\mathrm{AREA}_{\mathrm{I.S.}})$$

When the internal standard is the deuterated form of the analyte, the RF values are very close to 1.0. However, not every analyzed compound had a corresponding deuterated internal standard, and the RF value must be calculated. Extracted ion chromatograms are obtained for the characteristic ions for each of the compounds used for quantitative determination. The concentration of each component, is calculated using the following formula:

$$\mathrm{PAH\ (ng/cig.)} = \{[(\mathrm{AREA}_{\mathrm{analyte}}/\mathrm{AREA}_{\mathrm{I.S.}})/\mathrm{RF}] \cdot \mathrm{I.S.\ (ng)}\}/(\mathrm{No.\ of\ smoked\ cigs.})$$

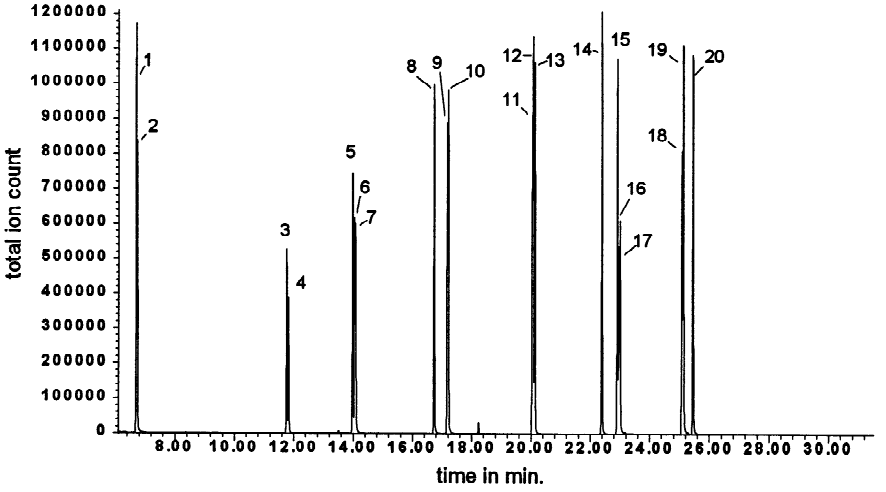

Fig. 2. SIM chromatogram for the standards and deuterated standards of PAHs in a 0.5 μg/ml solution. Peaks: 1=[$^2H_8$]-naphthalene, 2=naphthalene, 3=[$^2H_{10}$]-fluorene, 4=fluorene, 5=phenanthrene, 6=[$^2H_{10}$]-anthracene, 7=anthracene, 8=fluoranthene, 9=[$^2H_{10}$]-pyrene, 10=pyrene, 11=1,2-benzanthracene, 12=[$^2H_{12}$]-chrysene, 13=chrysene, 14=benzofluoranthene, 15=benzo[*e*]pyrene, 16=[$^2H_{12}$]-benzo[*a*]pyrene, 17=benzo[*a*]pyrene, 18=[$^2H_{14}$]-dibenz[*a,h*]anthracene, 19=dibenzanthracene, 20=benzoperylene.

SIM data collection allowed an increased sensitivity of about 10-fold over full scan detection.

Besides EI+ SIM detection for the mass spectrometer, it has been previously reported [37–40] that selected PAHs may be detected using negative chemical ionization (NCI) SIM. NCI SIM does not detect all PAHs, but the sensitivity of this type of detection is very good, and also generates a simpler chromatogram because the detection is more selective.

For NCI SIM detection, the same instrumentation as previously described was utilized, except that the MS instrument was equipped with the CI ionization source using a flow of CH_4 gas at 2 ml/min. A ZB1 column (12 m×0.25 mm I.D., 0.25 μm film thickness) was installed in the GC system. The injection temperature was 300°C, initial oven temperature 100°C, initial hold time 0.0 min, rate of temperature program 15°C/min, final oven temperature 310°C, final hold time 5 min. The carrier gas was helium. A pulse splitless injection of 1 μl was used, with pulse pressure of 30 p.s.i., constant flow of 2.2 ml/min, starting column head pressure 20 p.s.i., split valve flow 50 ml/min, and purge valve on time 0.5 min. The PAHs that can be detected using NCI SIM and the ions used for their detection are shown in Table 2.

2.3. Experimental conditions for phenol determination

For the analysis of phenols, a 1.0-ml aliquot of the SDE extract was placed in an autosampler vial and 10 μl of anhydrous pyridine and 200 μl of bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) were added. The vial was capped, heated at 76°C for 30 min, allowed to cool and injected into the GC–MS system (the same instrumentation as for PAH analysis) for analysis of the trimethylsilyl (TMS) derivatives.

The GC was equipped with an HP5 MS column

Table 2
Ions used for NCI SIM mass spectra acquisition for PAHs

PAH	*m/z*
Phenanthrene	178
Fluoranthene	202
1,2-Benzanthracene	228
Benzo[*b*]fluoranthene	252
Benzo[*k*]fluoranthene	252
Benzo[*a*]pyrene	252
[$^2H_{12}$]-Benzo[*a*]pyrene	264
Dibenz[*a,c*]anthracene	278
Dibenz[*a,h*]anthracene	278
[$^2H_{14}$]-Dibenz[*a,h*]anthracene	292
Benzoperylene	276

(30 m×0.25 mm I.D., 0.25 μm film thickness). The injection temperature was 280°C, initial oven temperature 45°C, initial hold time 5.0 min, rate of temperature program 10°C/min, final oven temperature 310°C, final hold time 5 min. The carrier gas was helium. A pulse splitless injection of 1 μl was used with pulse pressure 30 p.s.i., constant flow of 2.0 ml/min, staring column head pressure 16.5 p.s.i., split valve flow 50 ml/min, purge valve on time 1.0 min. Typical EI+ mass spectra of TMS derivatives of phenols were obtained from standards. For better sensitivity, SIM mass spectral detection was preferred and the ions selected for quantitation for each of the compounds analyzed are shown in Table 3. Table 3 indicates the hydroxybenzenes as used in the standard. Because the TMS group replaces an active hydrogen or deuterium, the ion or fragment selected for SIM measurement reflects this substitution. The SIM chromatogram for a solution of 0.5 μg/ml standards and deuterated standards of phenols is given in Fig. 3.

Except for the use of SDE as sample preparation step, the determination technique for phenols was adapted from the literature [18]. For the quantitation, peak areas of the analytes and of the corresponding internal standards were measured in the same manner as for PAHs analysis. Also, the same procedure based on the determination of the response factors (RFs) was applied. Not all phenols had a corresponding deuterated internal standard. For example, only [$^2H_8$]-*o*-cresol was used as a deuterated standard for cresols. Further, the concentration of each component, was calculated using the formula:

$$\text{Phenol}\ (\mu g/\text{cig.}) = \{[(\text{AREA}_{\text{analyte}}/\text{AREA}_{\text{I.S.}})/\text{RF}] \cdot \text{I.S.}\ (\mu g)\}/(\text{No. of smoked cigs.})$$

2.4. Experimental conditions for aromatic amine determination

The aromatic amines analysis was performed using derivatization with heptafluorobutyric anhydride (HFBA) of the SDE extract, followed by GC–MS analysis. For this purpose, 1.0 ml of the SDE extract was placed in an autosampler vial and treated with 10 μl of anhydrous pyridine and 2 μl of HFBA. The sample was heated at 76°C for 30 min, allowed to cool, and injected into the GC–MS system for analysis by SIM NCI GC–MS. The same instrumentation as applied for NCI analysis of PAHs was used. A 12 m HP-1 column (0.25 mm I.D., 0.25 μm film thickness) was used for separation. The injection temperature was 270°C, initial oven temperature 80°C, initial hold time 0 min, rate of temperature program 8°C/min, final oven temperature 310°C, final hold time 5 min. The carrier gas was helium. A pulse splitless injection of 1 μl was used, with pulse pressure of 30 p.s.i., constant flow at 2.0 ml/min, starting column head pressure 16.5 p.s.i., split valve flow of 50 ml/min, purge valve on time 0.5 min. The MS instrument was operated in the SIM NCI mode. For this purpose, similarly to the PAH detection using SIM NCI, a flow of CH_4 gas at 2 ml/min was used in the MS instrument, which was equipped with a CI source. NCI mass spectra of HFBA derivatives of aromatic amines show a predominant ion at M−20 (loss of HF) leading to good sensitivity. These mass spectra were obtained from standards. For quantitation, SIM mass spectral data for each of the derivatized compounds were collected in seven SIM groups. The ions used for quantitation are shown in Table 4.

The SIM chromatogram for a solution of 0.2 μg/ml standards and deuterated standards of aromatic amines is given in Fig. 4. The quantiation was done similarly as for PAHs and phenols, using the ratio of peak areas of the analytes and corresponding internal standards. The response factors were calculated for each analyte, and the concentration calculated based on a formula identical to that described for PAHs. Automatic calibration and

Table 3
Ions used for SIM mass spectra acquisition for phenols derivatized with BSTFA

Phenol	*m/z* for the TMS derivatives
Phenol	166
[$^2H_6$]-Phenol	171
o-Cresol	180
[$^2H_8$]-*o*-Cresol	187
m-Cresol	180
p-Cresol	180
Catechol	254
Resorcinol	254
Hydroquinone	254
[$^2H_6$]-Hydroquinone	258

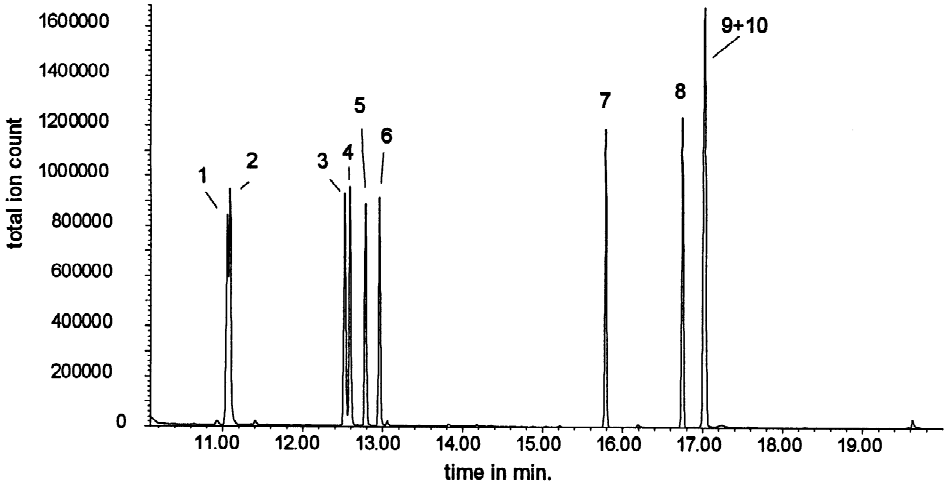

Fig. 3. SIM chromatogram for the standards and deuterated standards of phenols TMS derivatives in a 0.5 μg/ml solution of the initial phenols. Peaks: 1=[$^2H_6$]-phenol, 2=phenol, 3=[$^2H_8$]-*o*-cresol, 4=*o*-cresol, 5=*m*-cresol, 6=*p*-cresol, 7=catechol, 8=resorcinol, 9+10=[$^2H_6$]-hydroquinone+hydroquinone.

quantitation procedures can be implemented using data analysis software.

Table 4
Ions used for SIM mass spectra acquisition of aromatic amines derivatized with HFBA

Aromatic amine	*m/z* for the HFBA derivatives
Aniline	269
Aniline-d_5	274
o-Toluidine	283
[$^2H_7$]-*o*-Toluidine	290
m-Toluidine	283
p-Toluidine	283
2-Ethylaniline	297
3-Ethylaniline	297
4-Ethylaniline	297
2,4-Dimethylaniline	297
2,5-Dimethylaniline	297
1-Naphthylamine	319
2-Naphthylamine	319
[$^2H_7$]-2-Naphthylamine	326
3-Aminobiphenyl	345
4-Aminobiphenyl	345
[$^2H_9$]-4-Aminobiphenyl	354
Benzidine	556
[$^2H_8$]-Benzidine	564
Tolidine	584

3. Results and discussion

The SDE extract of smoke pads consists of a complex mixture of components. A chromatographic profile for the SDE extract of a 1R4F Kentucky reference cigarette obtained using the chromatographic conditions for the PAH analysis is shown in Fig. 5. The chromatogram is dominated by a nicotine peak, and contains a large number of other compounds found in smoke.

Particulate phase collected from 1R4F cigarettes was also processed by a procedure adapted from a method reported in the literature [2] for PAH analysis and using two processing steps. The first step is a clean-up operation using SPE and the second is a Sephadex separation. The chromatographic profile, obtained from the SPE/Sephadex extract of 1R4F cigarette smoke, using the same chromatographic conditions as for the SDE extract is shown in Fig. 6.

The chromatogram from Fig. 6 is dominated by a group of long chain hydrocarbons. Their collective

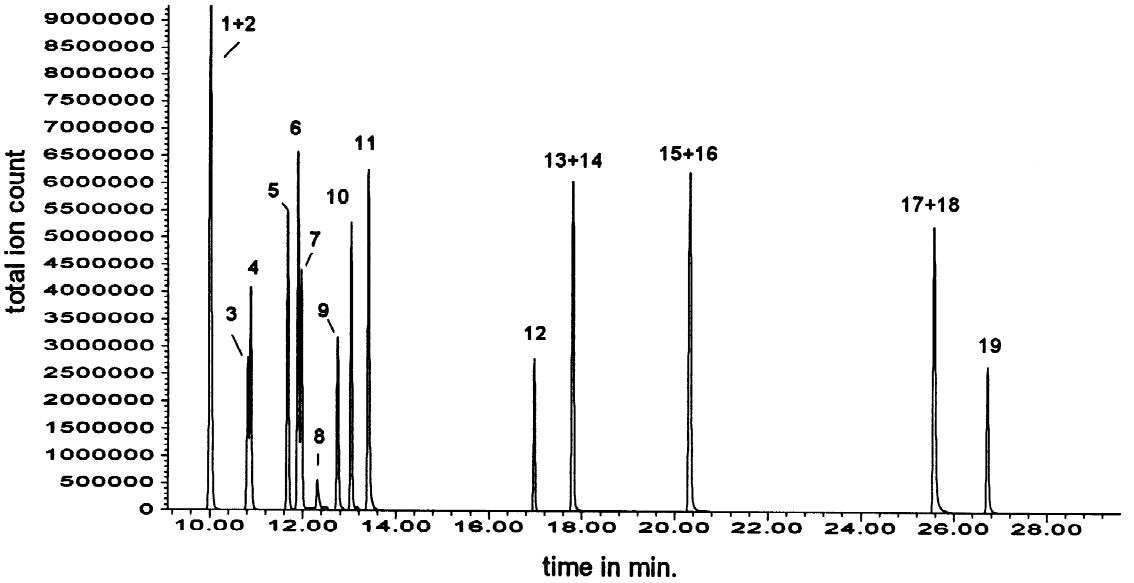

Fig. 4. SIM chromatogram for a solution of 0.2 μg/ml standards and deuterated standards of aromatic amines. Peaks: 1=aniline, 2=[$^2H_5$]-aniline, 3=[$^2H_7$]-*o*-toluidine, 4=*o*-toluidine, 5=*m*-toluidine, 6=*p*-toluidine, 7=2-ethylaniline, 8=2,5-dimethylaniline, 9=2,4-dimethylaniline, 10=3-ethylaniline, 11=4-ethylaniline, 12=1-naphthylamine, 13=2-naphthylamine, 14=[$^2H_7$]-2-naphthylamine, 15=4-aminobiphenyl, 16=[$^2H_9$]-4-aminobiphenyl, 17=benzidine, 18=[$^2H_8$]-benzidine, 19=tolidine.

spectrum for the interval 49.5 to 56.0 min indicates compounds of the type heneicosane, docosane, etc., by mass spectral library search.

By comparing Figs. 5 and 6, a very different composition can be expected for the matrix of the injected sample. The SPE/Sephadex chromatogram is rich in higher-molecular-mass compounds. These are more difficult to elute from the chromatographic column even at higher GC oven temperatures. This is a significant advantage of the SDE extract which elutes more completely from the column. Also, the SIM trace used for the measurement of PAHs is cleaner for the SDE extract. In addition to this, the preparation of the SDE extract is significantly less labor intensive as compared to the SPE/Sephadex procedure.

In the case of phenol analysis, an alternative procedure to SDE is the extraction of the smoke pads with *tert*.-butyl methyl ether (TBME). The samples are further analyzed by the same procedure as the SDE extract. Using TBME extraction, the trihydroxybenzenes (pyrrogallol and 1,2,4-trihydroxybenzene) can also be determined in the smoke extract. The trihydroxybenzenes do not distill using the SDE clean-up procedure and cannot be determined. Although this is a disadvantage for the SDE procedure, the advantages are the use of the same extract for all analyses, and the absence of molecules with higher boiling points in the extract which leads to a longer life of the chromatographic column.

The analysis in smoke of aromatic amines, is commonly done using an acid extraction of the pads, followed by a pH change and a second extraction in organic solvents of the aromatic amines. The advantage of the SDE procedure is the simplicity of the clean-up step, and again the use of the same extract already prepared for PAHs and phenol analysis. Amine analysis using the SDE procedure also leads to cleaner chromatograms.

3.1. Results for PAHs

The quantitative results for PAHs obtained using SDE extract and EI+ SIM detection as previously described, are given for three control cigarettes in Table 5. These cigarettes were Kentucky reference

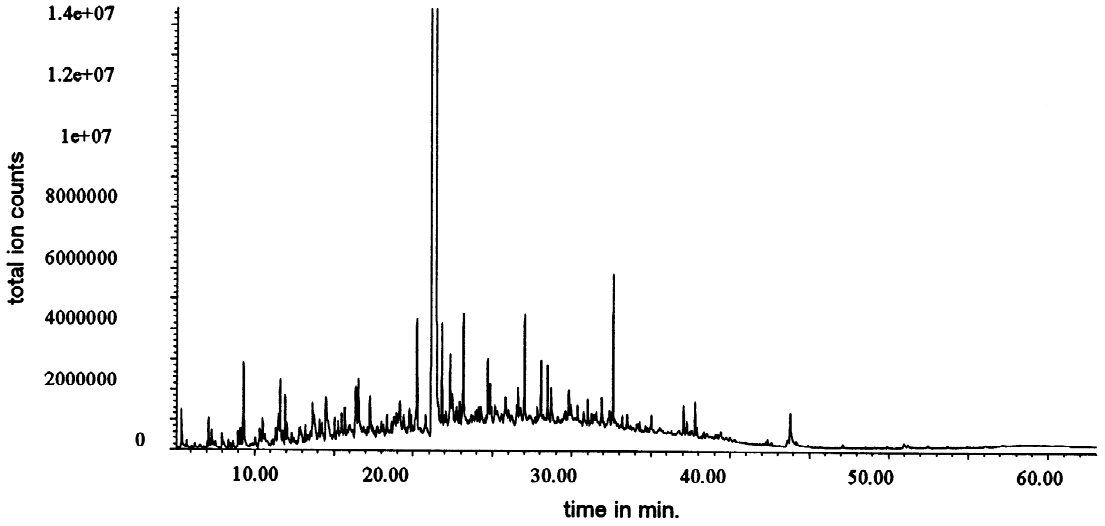

Fig. 5. The chromatogram for the SDE extract of a 1R4F Kentucky reference cigarette.

cigarettes 1R4F (for FTC smoking, average TPM = 11.0 mg), 1R5F (for FTC smoking, average TPM = 1.8 mg), and 1R3 (for FTC smoking, average TPM = 27.0 mg). As seen in Table 5, the relative standard deviations (RSDs) for various PAHs are within very good limits. Some compounds at very low levels (a few ng/cig.) have higher RSDs, as expected. The comparison of the detected levels for various PAHs shown in Table 5 for 1R4F Kentucky reference cigarettes with the results obtained by the alternative technique using SPE/Sephadex extraction as well as with some results reported in the literature can be seen in Fig. 7. As seen in Fig. 7, the agreement between the data is very good. For 1R5F cigarettes the available data in the literature [18] gave 1.3 ng/cig. for benzo[*a*]pyrene that is in good agreement

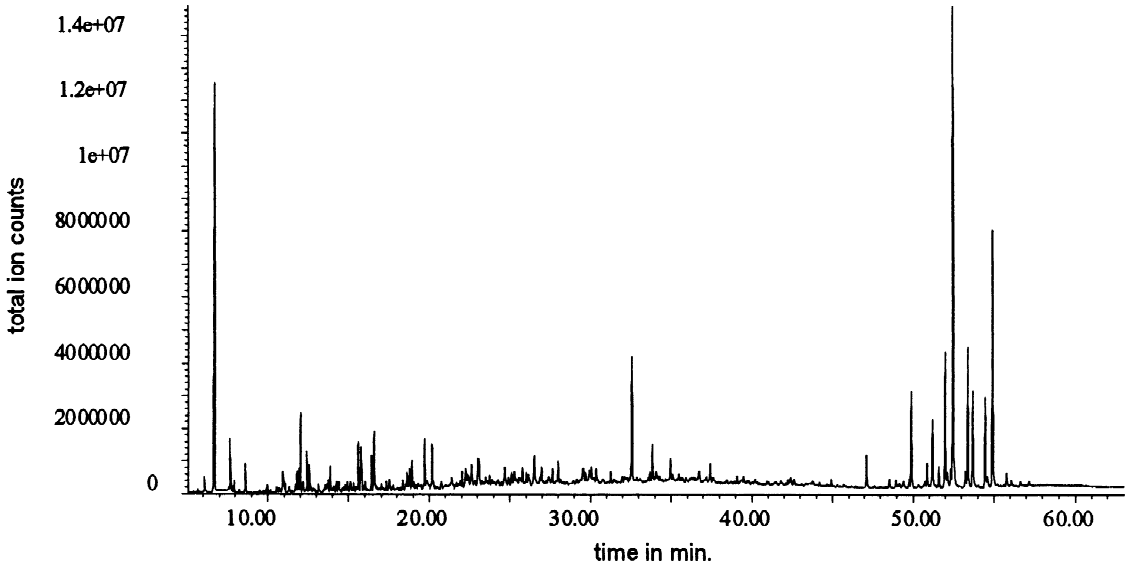

Fig. 6. The chromatogram for the SPE/Sephadex extract of a 1R4F Kentucky reference cigarette.

Table 5
PAH data obtained from Kentucky reference cigarettes expressed in ng/cig. (averages of four replicates)

	1R4F		1R5F		1R3	
	Average (ng/cig.)	RSD (%)	Average (ng/cig.)	RSD (%)	Average (ng/cig.)	RSD (%)
Naphthalene	361.7	3.1	57.5	1.9	893.2	3.8
Fluorene	239.0	1.6	33.8	1.3	584.5	1.5
Phenanthrene	147.7	3.0	31.0	1.9	366.3	1.7
Anthracene	35.8	2.6	13.9	2.2	88.9	1.9
Fluoranthene	51.6	4.6	16.2	1.5	126.7	1.7
Pyrene	32.1	3.3	10.2	2.2	80.0	3.1
2,3-Benzofluorene	35.3	2.8	9.9	1.3	83.4	4.4
1,2-Benzanthracene	14.0	2.6	3.0	8.0	32.7	8.5
Chrysene	11.2	3.0	4.7	4.5	27.5	7.0
Benzofluoranthene	11.2	3.0	3.2	3.1	26.6	8.0
Benzo[*e*]pyrene	6.4	5.9	2.0	8.5	15.1	2.1
Benzo[*a*]pyrene	7.6	2.9	1.6	8.8	18.4	3.7
Perylene	3.5	2.9	0.2	15.0	8.8	3.8
Dibenzanthracene[a]	2.3	9.1	0.3	6.7	5.6	4.6
Benzoperylene	2.3	7.8	0.4	5.0	5.2	7.5

[a] Note: Dibenzanthracene measured in this study is probably a mixture of dibenz[*a*,*c*]anthracene and dibenz[*a*,*h*]anthracene.

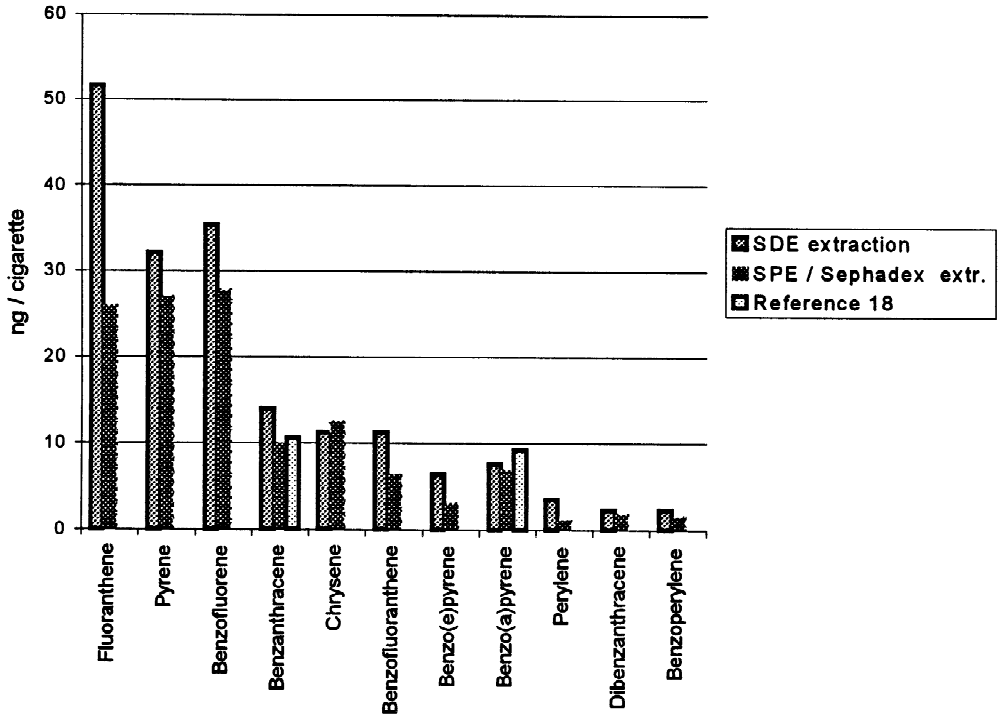

Fig. 7. The comparison of the results obtained by SDE procedure (in ng/cig.) and the results obtained by SPE/Sephadex extraction techniques or reported in the literature for 1R4F cigarette smoke.

with the data shown in Table X. No data for comparison were available for naphthalene, fluorene, phenanthrene and anthracene.

Regarding the results obtained using SIM NCI detection procedure, an example of extracted ion chromatogram from the SIM group for ions 252 and 264 used for quantitation of the SDE extract for a 1R4F cigarette is shown in Fig. 8.

The NCI SIM results obtained for benzo[a]pyrene levels in 1R4F were compared with the results obtained using EI+ SIM detection and are shown in Table 6. As seen in Table 6, the results for benzo[*a*]pyrene are in good agreement with those obtained using EI+ SIM, as expected.

Table 6
Comparison of the results on benzo[*a*]pyrene in 1R4F cigarettes using NCI SIM and EI+ SIM detection (ng/cig.)

	Average (ng/cig.)	RSD (%)
NCI SIM detection	7.4	4.2
EI+ SIM detection	7.6	2.9

3.2. Results for phenols

The phenol results obtained using SDE extract followed by silylation and EI+ SIM detection as previously described, are given for three control cigarettes in Table 7. The comparison of the data shown in Table 7 for 1R4F cigarettes with the results obtained by the alternative technique using TBME extraction, as well as the comparison with some results reported in the literature can be seen in Fig. 9. As seen in Fig. 9, the agreement between the data obtained by different techniques is very good. For 1R5F cigarettes the comparison of SDE results with those available in the literature [18] is shown in Fig. 10. As seen in Fig. 10, the agreement between the data obtained using different procedures is very good.

3.3. Results for aromatic amines

The levels of aromatic amines obtained using SDE extract and NCI SIM detection as previously described, are given for three control cigarettes in Table 8. As seen in Table 8, the procedure gives results with good relative standard deviation for 1R4F and for 1R3 cigarettes. The standard deviations are slightly higher for 1R5F cigarette. This is an Ultra Light cigarette, and the content of specific

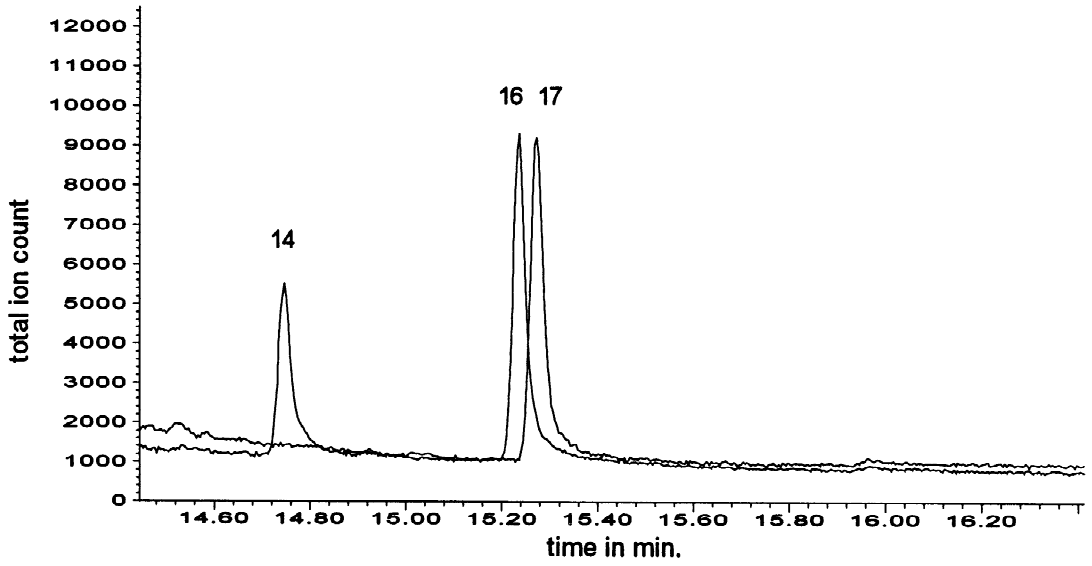

Fig. 8. Extracted ion chromatogram (from the SIM group) for ions 252 and 264 used for quantitation of the SDE extract for a 1R4F cigarette using NCI SIM detection. Peaks: 14=benzofluoranthene, 16=[$^{2}H_{12}$]-benzo[*a*]pyrene, 17=benzo[*a*]pyrene.

Table 7
Phenols data obtained from Kentucky reference cigarettes expressed in μg/cig. (averages of four replicates)

	1R4F		1R5F		1R3	
	Average (μg/cig.)	RSD (%)	Average (μg/cig.)	RSD (%)	Average (μg/cig.)	RSD (%)
Phenol	6.9	4.6	0.9	10.6	55.4	13.0
o-Cresol	2.8	5.0	0.2	17.7	16.9	3.1
m-Cresol	1.6	9.6	0.1	20.0	8.1	11.6
p-Cresol	3.7	12.4	0.2	15.0	16.1	12.3
Catechol	52.3	5.4	7.4	22.5	87.2	16.7
Resorcinol	1.8	8.2	0.6	18.9	2.7	6.0
Hydroquinone	35.6	15.3	4.9	14.3	70.5	8.8

analytes is low. This may explain higher RSD noticed for this cigarette.

The comparison of the data shown in Table 8 for 1R4F cigarettes with the results obtained by an alternative technique using acid extraction, pH change and second extraction in CH_2Cl_2 as well as with some results reported in the literature can be seen in Fig. 11. As seen in Fig. 11, the agreement between the data is very good. For 1R5F cigarettes the available data in the literature [18] gave 4 ng/cig. for 2-naphthylamine, and 1.3 for 4-aminobiphenyl, which are in fair agreement with the data shown in Table 8.

Comparing the results on particulate smoke analy-

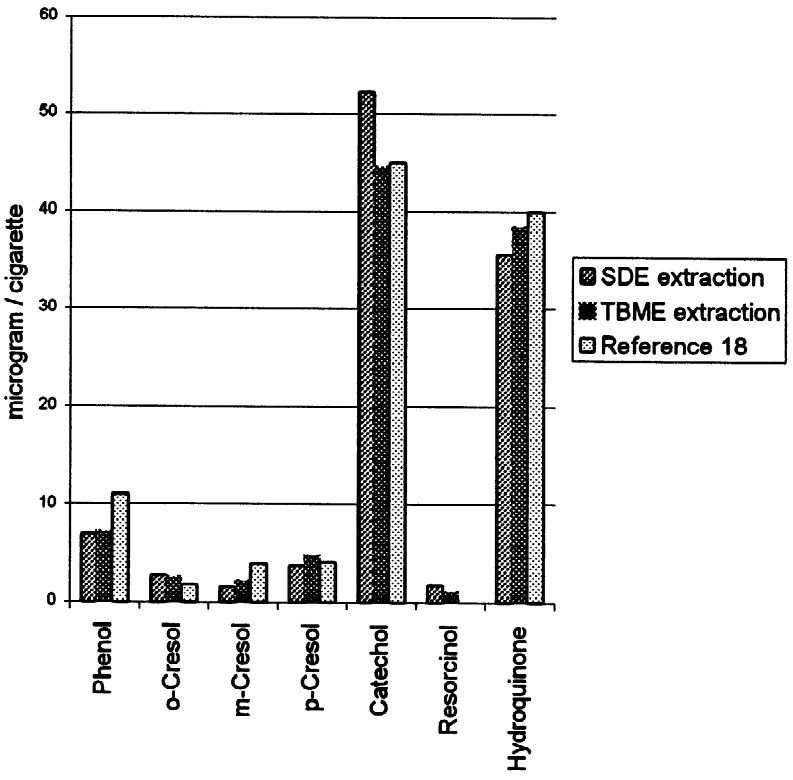

Fig. 9. The comparison of the results obtained on phenols by SDE procedure (in μg/cig.) and the results for 1R4F cigarette obtained by TBME extraction techniques or reported in the literature.

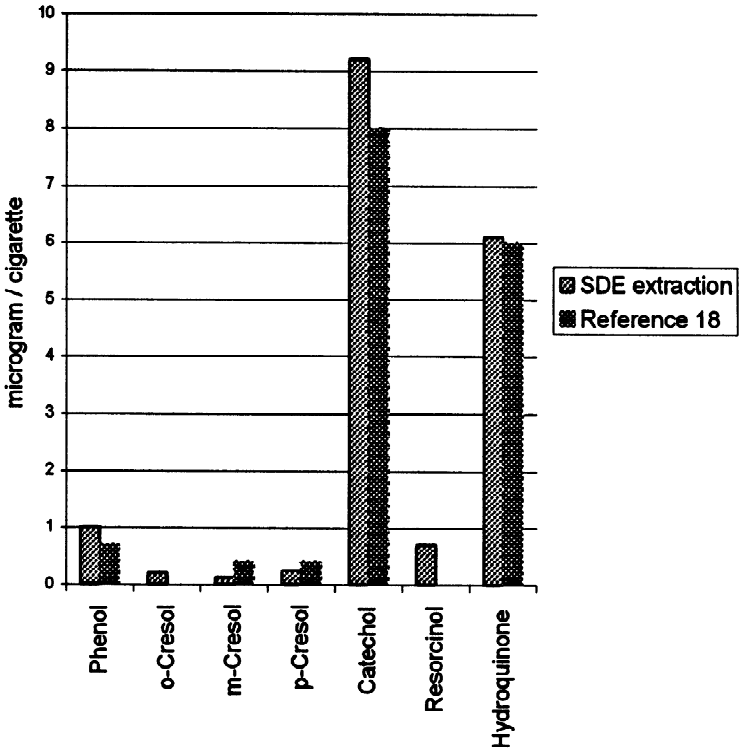

Fig. 10. The comparison of the results obtained on phenols by SDE procedure (in μg/cig.) and the results for 1R5F cigarette reported in the literature.

Table 8
Aromatic amine data obtained from Kentucky reference cigarettes expressed in ng/cig. (averages of four replicates)

	1R4F		1R5F		1R3	
	Average (ng/cig.)	RSD (%)	Average (ng/cig.)	RSD (%)	Average (ng/cig.)	RSD (%)
Aniline	212.4	4.4	34.6	3.5	562.8	4.3
o-Toluidine	39.8	2.5	6.3	4.9	95.6	0.9
m-Toluidine	49.0	6.2	7.7	5.0	134.9	4.6
p-Toluidine	47.3	2.8	7.4	2.3	111.8	3.1
2-Ethylaniline	3.6	4.5	0.6	4.8	8.0	5.4
2,5-Dimethylaniline	24.6	5.6	4.1	7.9	56.3	4.1
2,4-Dimethylaniline	18.4	3.3	2.7	6.7	43.5	2.5
3-Ethylaniline	15.3	2.4	2.5	5.1	38.4	5.1
4-Ethylaniline	9.4	5.2	1.5	9.3	20.8	3.4
1-Naphthylamine	9.3	3.5	1.6	5.7	23.5	6.7
2-Naphthylamine	9.8	2.8	1.7	3.0	24.3	6.5
3-Aminobiphenyl	6.3	5.2	1.1	15.2	16.9	4.1
4-Aminobiphenyl	5.4	9.0	0.8	11.1	12.7	8.7
Benzidine	2.2	11.1	0.4	5.3	4.3	8.8
Tolidine	1.3	10.4	0.2	23.8	2.5	10.5

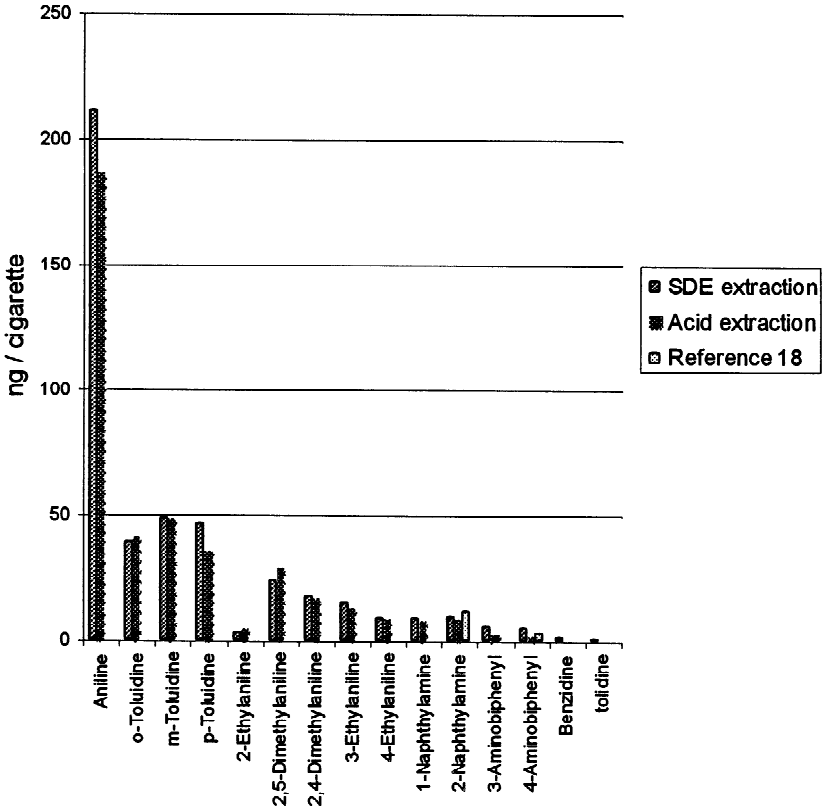

Fig. 11. The comparison of the results obtained by SDE procedure for aromatic amines (in ng/cig.) and the results obtained by acid extraction techniques or reported in the literature for 1R4F cigarette smoke.

sis for PAHs, phenols and aromatic amines using the SDE clean-up procedure with other results for the same samples but using different sample preparation techniques, very good agreement is noticed. However, the SDE procedure has significant advantages regarding the simplicity of the technique and the capability to use the same sample for multiple analyses.

References

[1] S.C. Moldoveanu, Analytical Pyrolysis of Natural Organic Polymers, Elsevier, Amsterdam, 1998.
[2] J.B. Forehand, G.L. Dooly, S.C. Moldoveanu, in: 53rd Tobacco Science Research Conference, Montreal, 12 September 1999.
[3] R.J. Levins, Chromatographia 11 (1978) 736.
[4] J.E. Marriott, A.S. Weaving, in: 31st Tobacco Chemists' Research Conference, Greensboro, NC, 5 October 1977.
[5] M.N. Kyali, S. Rubio-Barroso, J. Liq. Chromatogr. 18 (1995) 1617.
[6] E.L. Wynder, D. Hoffmann, Tobacco and Tobacco Smoke, Academic Press, New York, 1986.
[7] R.E. Allen, in: 30th Tobacco Chemists' Research Conference, Nashville, TN, 20 October 1976.
[8] J. Dumont, F. Larocque-Lazure, C. Iorio, J. Chromatogr. Sci. 31 (1993) 371.
[9] C.H. Risner, J. Chromatogr. Sci. 26 (1988) 113.
[10] M.L. Lee, M. Novotny, K.D. Bartle, Anal. Chem. 48 (1976) 405.
[11] E.J. Nanni, M.E. Lovette, R.D. Hicks, K.W. Fowler, M.F. Borgerding, J. Chromatogr. 505 (1990) 365.
[12] B.A. Tomkins, R.A. Jenkins, W.H. Griest, R.R. Reagan, J. Assoc. Off. Anal. Chem. 67 (1984) 919.
[13] C.H. Risner, S.H. Cash, J. Chromatogr. Sci. 28 (1990) 239.
[14] M.E. Snook, W.S. Schlotzhauer, W.J. Chamberlain, Tobacco Sci. XXII (1978) 106.
[15] J. Arnarp, S. Broman, B.-M. Dahlin, O. Dahlman, C.R. Enzell, T. Pettersson, Acta Chem. Scand. 45 (1991) 529.

[16] R.F. Arrendale, R.F. Severson, O.T. Chortyk, M.E. Snook, J. Chromatogr. Sci. 20 (1982) 136.
[17] G. Jeanty, J. Massé, P. Bercot, Beitr. Tabakforsch. Int. 12 (1984) 245.
[18] M.F. Borgerding, J.A. Bodnar, H.L. Chung, P.P. Mangan, C.C. Morrison, C.H. Risner, J.C. Rogers, D.F. Simmons, M.S. Uhrig, F.N. Wendelboe, D.E. Wingate, L.S. Winkler, Food Chem. Toxicol. 36 (1997) 169.
[19] C. Patrianakos, K.D. Brunemann, D. Hoffmann, in: 31st Tobacco Chemists' Research Conference, Greensboro, NC, 5 October 1977.
[20] H. Kataoka, J. Chromatogr. A 733 (1996) 19.
[21] C.F. Poole, S.K. Poole, J. Chromatogr. Sci. 25 (1987) 434.
[22] K. Kijima, H. Kataoka, M. Makita, J. Chromatogr. A 738 (1996) 83.
[23] G. Skarping, L. Renman, B.E.F. Smith, J. Chromatogr. 267 (1983) 315.
[24] G. Skarping, L. Renman, M. Dalene, J. Chromatogr. 270 (1983) 207.
[25] R.T. Coutts, E.E. Hargesheimer, F.M. Pasutto, G.B. Baker, J. Chromatogr. Sci. 19 (1981) 151.
[26] H.-B. Lee, J. Chromatogr. 457 (1988) 267.
[27] D.E. Bradway, T. Shafik, J. Chromatogr. Sci. 15 (1977) 322.
[28] S. Likens, G. Nickerson, Proc. Am. Soc. Brew. Chem. (1964) 5.
[29] M. Godefroot, P. Sandra, M. Verzele, J. Chromatogr. 203 (1981) 325.
[30] T.H. Schultz, R.A. Flath, T.R. Mon, S.B. Eggling, R. Teranishi, J. Agric. Food Chem. 25 (1977) 446.
[31] S.C. Moldoveanu, J.L. Roles, Q. Zha, in: 50th Tobacco Chemists' Research Conference, Richmond, VA, 1996, Paper No. 42.
[32] H.C. Pillsbury, C.C. Bright, K.J. O'Connor, F.W. Irish, J. Assoc. Off. Anal. Chem. 52 (1969) 458.
[33] Routine Analytical Cigarette Smoking Machine – Definitions and Standard Conditions, International Standard Organization, Geneva, 1991, ISO 3308:1991 (E).
[34] Tobacco and Tobacco Products – Atmosphere for Conditioning and Testing, International Standard Organization, Geneva, 1991, ISO 3402:1991 (E).
[35] Cigarettes – Determination of Total and Nicotine Free Dry Particulate Matter Using a Routine Analytical Smoking Machine, International Standard Organization, Geneva, 1991, ISO 4387:1991 (E).
[36] G.N. Connoly, H. Saxner, Memorandum, The Commonwealth of Massachusetts, Exec. Office of Health and Human Services, 19 August 1997.
[37] M. Oehme, S. Mano, H. Stray, J. Chromatogr. 279 (1983) 649.
[38] M. Oehme, Int. J. Mass Spectrom. Ion Phys. 48 (1983) 287.
[39] M. Oehme, Chemosphere 14 (1985) 1285.
[40] G.K. Low, G.E. Batley, Biomed. Environ. Mass Spectrom. 13 (1986) 95.