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ANALYSIS OF TRICHOTHECENE MYCOTOXINS IN HUMAN BLOOD BY CAPILLARY COLUMN GAS CHROMATOGRAPHY–AMMONIA CHEMICAL IONIZATION MASS SPECTROMETRY

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SUMMARY

Capillary column gas chromatography–ammonia chemical ionization mass spectrometry was found to be an excellent technique for the trace detection and identification of underivatized trichothecene mycotoxins. Abundant $(M + H)^+$ and/or $(M + NH_4)^+$ pseudo-molecular ions were observed for T-2 toxin, HT-2 toxin, T-2 triol, diacetoxyscirpenol, deoxynivalenol and verrucarol under the conditions developed. This method was successfully applied to the analysis of human blood samples spiked with mycotoxins in the 0–500 ng/g range during a recent interlaboratory exercise. T-2 toxin and diacetoxyscirpenol were detected in these samples in the 2–180 ng/g range. Detection limits of 0.7 and 3.6 ng/g for T-2 toxin and diacetoxyscirpenol, respectively, were possible owing to the specificity of the method.

INTRODUCTION

Trichothecene mycotoxins are a group of naturally occurring sesquiterpenoid compounds produced by various species of imperfect fungi. The defence science community became interested in mycotoxins owing to reports of their alleged use as chemical warfare agents in Southeast Asia[1–3]. These "yellow rain" allegations have been supported by the findings of Rosen and Rosen[4] and Mirocha[5]. Rosen and Rosen[4] found the mycotoxins deoxynivalenol (DON), diacetoxyscirpenol (DAS), T-2 toxin (T2) and zearalenone (F2) in a sample of yellow powder scraped from vegetation by Hmong resistance fighters in the Phou Bia area. Mirocha[5] detected DAS, DON, T2 and F2 in leaves, water and yellow powder obtained from "yellow rain" attack sites in Southeast Asia. In addition T2 and HT-2 toxin (HT2), a metabolite of T2 in animals, were found in biological fluids of alleged victims[5].

The need for routine agricultural monitoring and the possible use of mycotoxins as chemical warfare agents have resulted in the development of a number of analytical techniques for their detection. These methods include thin-layer chromatography[6], high-performance liquid chromatography (HPLC)[7–12], supercritical fluid chromatography (SFC)[13–15], tandem mass spectrometry[16,17] and gas chromatography (GC)[4,5,18–35]. Gas chromatography–mass spectrometry (GC–MS) methods

are often favoured owing to instrument availability and the sensitivity and specificity of these methods. Most reported GC–MS methods utilize derivatization with trimethylsilylacetamide, heptafluorobutyrylimidazole or another derivatizing agent prior to analysis. However, a number of laboratories[17,34,35] have recently demonstrated the ability to detect mycotoxins in an underivatized state using fused-silica capillary columns.

We report the development and application of a capillary column GC–MS method for the trace determination of mycotoxins that does not require mycotoxin derivatization. MS determinations were performed under ammonia chemical ionization (CI) conditions, a technique recently reported for HPLC–MS[8,10] and SFC–MS[14] analysis of mycotoxin standards. Abundant $(M + H)^+$ and/or $(M + NH_4)^+$ pseudo-molecular ions were observed under the conditions selected with considerably less fragmentation than was observed during electron-impact ionization. This method was applied to the analysis of twenty human blood samples spiked with mycotoxins in the 0–500 ng/g range as part of an interlaboratory exercise designed to evaluate procedures. T2 and DAS were detected in these samples at levels ranging from 2 to 180 ng/g. Sample detection limits of 0.7 and 3.6 ng/g were estimated for the determination of T2 and DAS, respectively. The results of the other laboratories are presented for comparative purposes.

EXPERIMENTAL

Mycotoxin standards

The mycotoxin standards were prepared in "HPLC grade" acetone and stored in PTFE-lined screw-topped glass vials. DAS, DON and T2 were purchased from Myco-Labs (Chesterfield, MO, U.S.A.). VER, HT2 and T2 were obtained from Sigma (St. Louis, MO, U.S.A.).

Instrumental analysis

Capillary column GC–flame ionization detection (FID) analyses were carried out on two instruments. Most GC–FID chromatograms were obtained using a Varian 6000 (Varian Assoc., Georgetown, Canada) gas chromatograph equipped with a J + W on-column injector (J + W Scientific, Rancho Cordova, CA, U.S.A.). Varian 6000 GC conditions were as follows: 15 m × 0.32 mm I.D. 0.25 μm J + W DB-1 capillary column; ambient temperature injection followed by a temperature programme of 75°C (2 min) 10°C/min to 300°C (10 min). Additional GC–FID chromatograms were obtained using a Varian 3700 equipped with an on-column injector of our own design[36]. Varian 3700 conditions were as follows: 15 m × 0.32 mm I.D. 0.25 μm J + W DB-5 capillary column; temperature programme of 50°C (2 min) 10°C/min to 300°C (8 min). High purity helium, at a linear velocity of 35 cm/s, was used as the carrier gas.

Capillary column GC–MS analyses were performed with a VG Micromass 70/70E mass spectrometer (VG Analytical, Wythenshawe, U.K.) equipped with a Varian 3700 gas chromatograph. Chromatographic conditions were the same as those used for Varian 3700 FID study. The direct interface was modified to permit the capillary column to enter the ion source.

Anhydrous grade ammonia (99.99%) was used as the reagent gas for capillary

column–ammonia chemical ionization (CI) MS analyses. The pressure near the source was $5 \cdot 10^{-5}$ Torr. The accelerating voltage was 6 kV, the electron energy 50 eV, the emission current 500 μA and the source temperature 160°C. Full scanning mass spectra were obtained from 550 to 20 u with a scan rate of 1 s/decade. $(M + NH_4)^+$ and $(M + 1 + NH_4)^+$ ions were monitored during accelerating voltage selected-ion monitoring (SIM) of the blood extracts for T2, HT2 and DAS. $(M + H)^+$ and $(M + 1 + H)^+$ ions were monitored for T-2 triol, $(M + H)^+$ and $(M - OH)^+$ for VER, and $(M + H)^+$ and $(M + NH_4)^+$ for DON during SIM analysis.

Blood samples

Twenty 5-ml human blood samples, spiked with an undisclosed number of mycotoxins in the 0–500 ng/g range, and 100 ml of blank blood were supplied by the Centre for Disease Control, Atlanta, GA, U.S.A. The blood samples were stabilized with heparin and 0.5% sodium fluoride prior to delivery and stored at 4°C for four months prior to clean-up and analysis.

Blood clean-up

Blood samples and blanks were taken through Black and Read's clean-up scheme for mycotoxins in blood[32]. A brief description follows. Whole blood (5 ml) was shaken vigorously with 10 ml of acetone and centrifuged, and the supernatant was decanted off. Acetone in the supernatant was removed under a gentle stream of nitrogen. The sample was loaded onto a conditioned C_{18} Sep-Pak (Waters Assoc., Milford, MA, U.S.A.), rinsed with 2 ml of water, and eluted with 2 ml of 40:60 methanol–water. This fraction contains the more polar mycotoxins. The C_{18} Sep-Pak was further eluted with 3 ml of 90:10 methanol–water. Water (2.5 ml) was added to this eluent, which contains the less polar mycotoxins. This fraction was extracted with two 5-ml volumes of methylene chloride and dried through 2 g of sodium sulphate. The C_{18} Sep-Pak fractions were combined, evaporated to dryness and taken up in 100 μl of acetone prior to analysis.

RESULTS AND DISCUSSION

Capillary column GC–FID

Most of the existing GC analysis methods use sample derivatization prior to mycotoxin detection. Heptafluorobutyryl derivatives have been used with electron-capture detection (ECD) to quantitate mycotoxins in grains[19,22,24,28] and plasma[27,33]. Trimethylsilyl derivatization has been reported for mycotoxin quantitation in food and/or feeds[20,30,31] with FID. The elimination of derivatization was attractive since it would save time during sample preparation and minimize the potential losses inherent in an additional handling step. In addition, concerns about derivative stability have been expressed, and several reports[19,22,24,28] suggest same-day analysis. For these reasons we developed a GC method to analyse mycotoxins in an underivatized state.

During preliminary capillary column GC–FID analysis, the mycotoxin standards displayed poor peak shape, often with significant tailing. The high polarity of the methanol solvent was suspected since the standards were believed to be at least 95% pure. In an attempt to provide better chromatographic peak shape, methanol

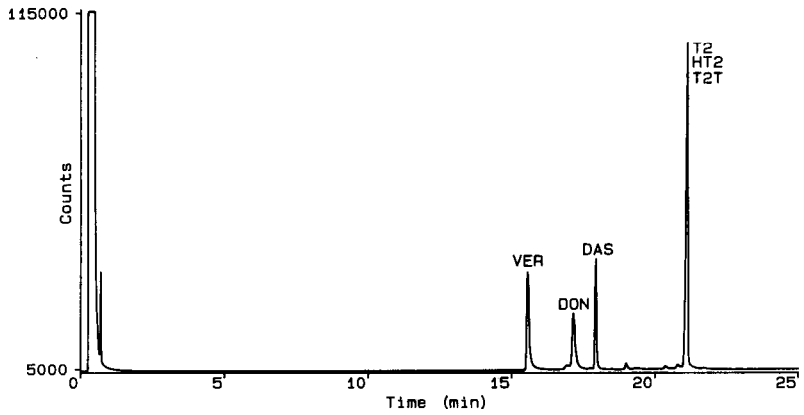

Fig. 1. Capillary column GC–FID chromatogram of 80 ng of VER, DON, DAS, T2, HT2 and T-2 triol (T2T). [11 · 10^{-11} A full scale; 75°C (2 min) 10°/min 300°C (10 min); 15 min × 0.32 mm I.D. DB-1].

solutions of the standards were co-injected with a chloroform plug[37]. The presence of chloroform resulted in better peak shape. Continued solvent investigations indicated that a further improvement in peak shape could be obtained with acetone. Acetone was selected as the solvent on the basis of this chromatographic evidence.

Fig. 1 illustrates a capillary column GC–FID chromatogram for the six mycotoxins used for this study. T2, HT2 and T-2 triol co-eluted on the 15 m DB-1 column. However, slight differences in retention time on the DB-5 column and more importantly, marked MS differences, permitted independent detection of these three mycotoxins by capillary column–ammonia CI MS. The DB-5 retention order was the same as reported by Miles[35]: T2, then HT2 and finally T-2 triol.

Clean-up scheme

The clean-up scheme[32] was evaluated by capillary column GC–FID with 5-ml

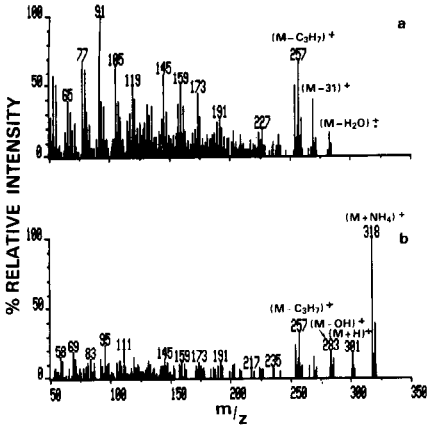

Fig. 2. (a) EI and (b) ammonia CI mass spectra of chlorinated-verrucarol obtained during capillary column GC–MS analysis.

aliquots of water and blood spiked with 10, 2.5 and 1 μg of VER, DAS and T2. DAS and T2 were recovered from water in the 52–72% (n = 6) and 61–76% (n = 6) range, respectively, for duplicate spikes at each level. The spiking level did not appear to affect recovery efficiency.

A peak with a slightly longer retention time was noted in place of or with VER in spiked water extracts. The electron-impact (EI) mass spectrum of this compound was somewhat ambiguous since there was no evidence of a molecular ion. However, both $(M + H)^+$ and $(M + NH_4)^+$ pseudo-molecular ions were observed during capillary column–ammonia CI MS analysis. It was evident from the isotopic pattern that a chlorine was present and that the molecular weight of the unknown was greater than that of verrucarol by 34 mass units. This compound was tentatively identified as a chlorinated-verrucarol on the basis of this and fragmentation evidence. Fig. 2 illustrates the mass spectra obtained and Fig. 3 illustrates a typical capillary column GC–FID chromatogram of a spiked water extract containing this compound. It was determined, through spiking experiments, that chlorinated-verrucarol was formed in small amounts during the methylene chloride extraction clean-up step. The subsequent sodium sulphate drying step appeared to increase conversion to chlorinated-verrucarol. Total disappearance of verrucarol after clean-up of spiked water was not uncommon.

A final evaluation of the clean-up scheme was done by spiking blank blood with VER, DAS and T2. Fig. 4 illustrates a typical capillary column GC–FID chromatogram of a 10-μg spiked blood extract. DAS and T2 were recovered at 30 ± 10% (n = 3) and 50 ± 10% (n = 3), respectively. Similar recoveries of T2 and DAS were observed during subsequent capillary column–ammonia CI MS analysis of the 2.5 and 1 μg spiked blood extracts. Recoveries of T2 and DAS were similar to those published for this clean-up scheme[32].

Neither verrucarol or chlorinated-verrucarol was observed in the spiked blood by capillary column GC–FID or GC–MS when the clean-up scheme was employed. Decomposition or reaction during blood clean-up was suspected since it was possible

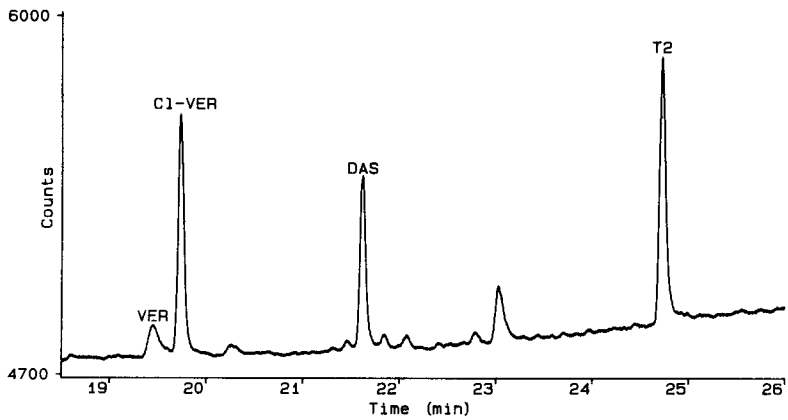

Fig. 3. Capillary column GC–FID chromatogram of 10 μg spike of VER, DAS and T2 in 5 ml of water after clean-up. Note the presence of chlorinated-verrucarol (Cl-VER). [1.5 · 10^{-11} A full scale; 50°C (2 min) 10°/min 300°C (8 min); 15 m × 0.32 mm I.D. DB-5.]

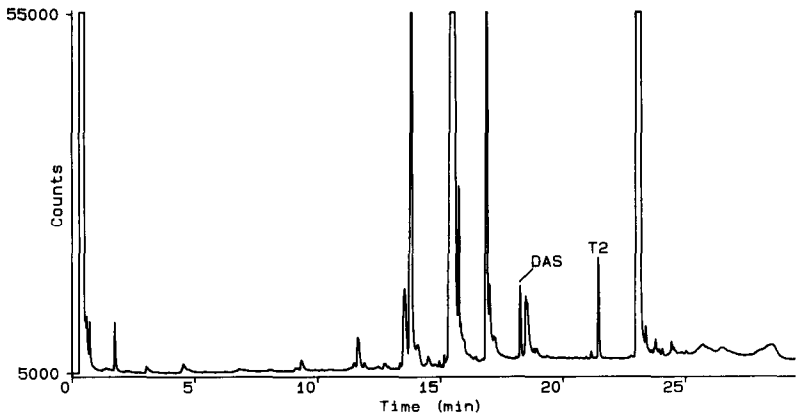

Fig. 4. Capillary column GC–FID chromatogram of 10 μg spike of VER, DAS and T2 in 5 ml of blood after clean-up. VER was not detected. [6 × 10^{-11} A full scale; 75°C (2 min) 10°/min 300°C (10 min); 15 m × 0.32 mm I.D. DB-1.]

to detect VER and chlorinated-verrucarol during co-injection with a blood blank extract. As a result, we were not able reliably to detect VER in blood using this scheme.

Capillary column GC–MS

Capillary column GC–MS under EI ionization conditions[38] was a satisfactory technique for μg/g mycotoxin determinations in blood. However, for trace detection there were considerable problems owing to the lack of molecular and higher molecular weight fragmentation ions.

Reports of $(M + H)^+$ and/or $(M + NH_4)^+$ pseudo-molecular ions[8,10,14] dur-

TABLE I

DEPENDENCE OF RELATIVE ION INTENSITY ON SOURCE TEMPERATURE FOR T2, DAS AND VER DURING CAPILLARY COLUMN–AMMONIA CI MS

Compound	*m/z*	*Relative intensity (%)*				
		140°C	*160°C*	*180°C*	*200°C*	*220°C*
T2	484 $(M + NH_4)^+$	100	100	58	35	20
	364	12	16	29	23	18
	122	50	95	100	100	100
DAS	384 $(M + NH_4)^+$	100	100	100	72	42
	306	13	24	43	47	62
	109	40	35	74	100	100
VER	284 $(M + NH_4)^+$	30	16	6	4	ND*
	267 $(M + H)^+$	78	35	27	17	10
	249	100	100	100	100	100
	231	52	60	58	54	53

* Not detected.

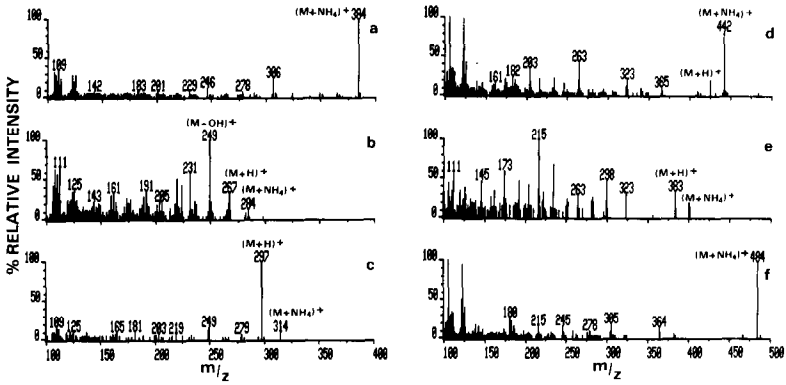

Fig. 5. Ammonia CI mass spectra of (a) DAS, (b) VER, (c) DON, (d) HT2, (e) T-2 triol and (f) T2, obtained during GC–MS analysis.

ing HPLC–MS and SFC–MS initiated the development of a capillary column–ammonia CI MS method. Recent ammonia CI experiences[39,40] suggested the use of maximum CI gas pressures and lower source temperatures. Considerable peak tailing, probably due to the low volatility of the mycotoxins, was observed at source temperatures below 140°C. Higher source temperatures reduced the peak tailing. However, the relative abundance of the pseudo-molecular ions decreased substantially. Table I illustrates these findings for T2, DAS and VER at source temperatures ranging from 140 to 220°C. A source temperature of 160°C was selected as it provided reasonable peak shape and good pseudo-molecular ion abundance.

Fig. 5 illustrates the ammonia CI mass spectra of the six mycotoxins studied. Abundant $(M + H)^+$ and/or $(M + NH_4)^+$ pseudo-molecular ions were observed for all the mycotoxins with considerably less fragmentation than under EI conditions. The ammonia CI mass spectra were similar to those obtained by HPLC–MS and SFC–MS. Table II compares the major ammonia CI ions for four trichothecene mycotoxins. T-2 triol and VER were not included in the other studies.

ABLE II

OMPARISON OF MAJOR AMMONIA CI IONS OBTAINED WITH DIFFERENT METHODS

ycotoxin	*Mol. wt.*	*GC–MS (this study)*		*Belt HPLC–MS*[10]		*Thermospray HPLC–MS*[8]		*SFC–MS*[13]	
		m/z	*RI (%)*	*m/z*	*RI (%)*	*m/z*	*RI (%)*	*m/z*	*RI (%)*
	466	484	100	484	100	484	100	484	100
T2	424	442	82	442	100	442	100	Not	
		425	22	425	20	358	9	available	
		323	20	342	17				
		263	42	323	12				
AS	366	384	100	384	100	384	100	384	100
		306	24	307	12				
ON	296	314	15	Not		314	98	314	100
		297	100	available		297	100	297	48
		249	18			284	58		

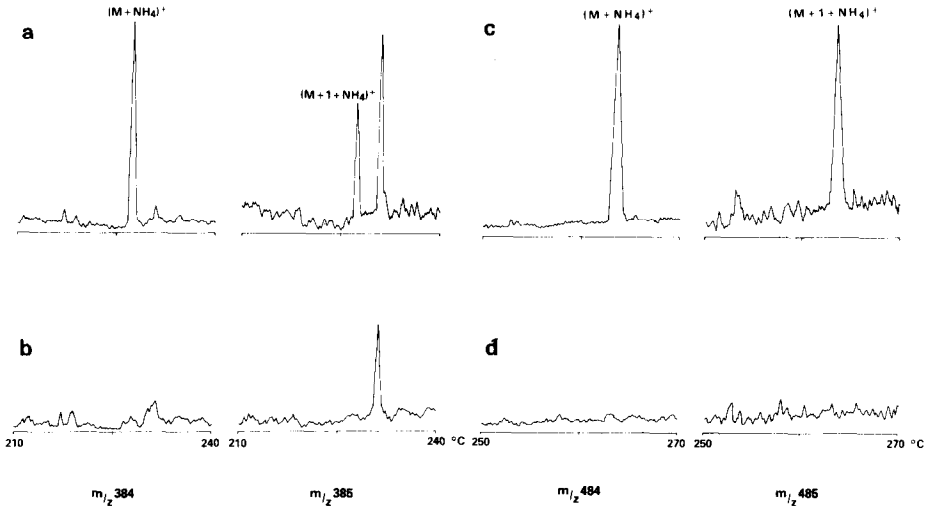

Fig. 6. (a) SIM determination of DAS in blood at 9.9 ng/g by capillary column–ammonia CI MS and (b) corresponding blood blank; (c) SIM determination of T2 in blood at 2.2 ng/g by capillary column–ammonia CI MS and (d) corresponding blood blank. [50°C (2 min) 10°/min 300°C (8 min); 15 m × 0.32 mm I.D. DB-5.]

Full scanning CI mass spectra were obtained with as little as 10 ng of mycotoxin. SIM afforded standard detection limits of 20, 30, 80, 130, 530 and 600 pg (signal-to-noise ratio $\geq$ 3:1) for T2, DAS, HT2, VER, T-2 triol and DON, respectively, based on the detection of two characteristic ions. These detection limits would improve by a factor of four or five if tentative identification, based on only one ion, was considered.

Application

Twenty blood samples, spiked with mycotoxins in the 0–500 ng/g range were taken through the clean-up scheme along with blood blanks. Seven of the samples (randomly selected) were not taken through the methylene chloride–sodium sulphate step for comparative purposes. All clean-up extracts, including blanks, were screened for the presence of mycotoxins by the capillary column–ammonia CI MS method developed. Confirmation was based on both a GC retention time match and relative ion abundance match of the SIM traces with mycotoxin standards. External standard quantitation was used for the duplicate analysis of each sample extract.

Detection limits were slightly better for extracts not taken through the methylene chloride–sodium sulphate clean-up step owing to decreased background currents. We estimate sample detection limits (signal-to-noise ratio $\geq$ 3:1) of 0.7 ng/g and 3.6 ng/g without this step for T2 and DAS, respectively, based on the SIM detection of two characteristic ions.

T2 and DAS were detected in the 2–180 ng/g range in the blood clean-up extracts. Fig. 6 illustrates the trace detection of T2 and DAS in human blood extracts B2 and A4, respectively, using the method developed. Table III lists the T2 and DAS findings of this laboratory and laboratories A and B. The results of laboratories A

TABLE III

COMPARISON OF T2 AND DAS DATA OBTAINED BY THE THREE LABORATORIES

Sample number	*Mycotoxin concentration (ng/g)*							
	T2				*DAS*			
	Spike level	*A*	*B*	*This lab**	*Spike level*	*A*	*B*	*This lab**
A1	200	205	400	125	10	4	12	12
A2	200	227	470	116	10	5	12	13
A3**	200	224	380	130	10	4	9	12
A4	200	217	270	171	10	4	11	9.9
B1	40	24	32	41	2	1	1	ND
B2	40	23	33	33	2	1	1	2.2***
B3	40	40	70	38	2	8	1	3.1***
B4	40	20	33	31	2	7	1	2.1***
C1**	10	8.9	8	2.8	200	91	220	38
C2	10	12	7	9.9	200	138	230	99
C3**	10	6.6	11	10.5	200	94	250	67
C4	10	12	11	9.2	200	130	230	165
D1**	0	ND§	ND	ND	0	ND	ND	ND
D2	0	ND	ND	ND	0	ND	ND	ND
D3	0	ND	ND	ND	0	ND	ND	ND
D4**	0	ND	ND	ND	0	ND	ND	ND
E1	2	2.9	3	2.1	40	25	40	38
E2	2	1.9	2	2.9	40	1.8	40	50
E3**	2	2.0	1	2.4	40	21	40	43
E4**	2	2.7	4	2.4	40	21	40	38

* No correction for clean-up scheme recovery efficiency.
** Methylene chloride–sodium sulphate step not used during clean-up by this laboratory.
*** Based on the detection of only the $(M + NH_4)^+$ ion.
§ ND = not detected.

and B were based on the GC–MS detection of heptafluorobutyryl and pentafluoropropionyl derivatives, respectively. All laboratories were in agreement as to the relative amounts of T2 and DAS and no false positives were reported.

CONCLUSIONS

The capillary column–ammonia CI MS method developed was found to be an excellent technique for the trace detection of underivatized trichothecene mycotoxins. Abundant $(M + H)^+$ and/or $(M + NH_4)^+$ ions were observed for T-2 toxin, HT-2 toxin, T-2 triol, diacetoxyscirpenol, deoxynivalenol and verrucarol under the conditions suggested.

This method was successfully applied to the analysis of mycotoxins in blood during a recent interlaboratory exercise. T-2 toxin and diacetoxyscirpenol were detected in these samples at levels ranging from 2 to 180 ng/g. Sample detection limits of 0.7 ng/g and 3.6 ng/g were estimated for T2 and DAS, respectively.

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