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Determination of organo-zinc based fungicides in timber treatments employing gas chromatographic analysis with mass selective detection and/or inductively coupled plasma atomic emission spectroscopy

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Abstract

A method for the determination of zinc octoate (zinc 2-ethylhexanoate) and acypetacs zinc in occupational hygiene samples and wood treatments formulations is described. The zinc carboxylates are liquid–liquid partitioned between toluene and 1 *M* HCl, with the liberated acids being extracted into the toluene and zinc (chloride) into the acid. The carboxylic acids are then methylated using trimethylsilyldiazomethane–methanol and the resultant methyl esters are selectively and sensitively analysed by gas chromatography with mass selective detection (GC–MS). Alternatively, the zinc content of the acid extract can be analysed by inductively coupled plasma atomic emission spectroscopy (ICP–AES). GC–MS is the preferred method of analysis for zinc octoate, where a single analyte (methyl-2-ethylhexanoate) is produced for analysis. Because acypetacs zinc contains a complex mixture of carboxylates, quantitative GC–MS analysis of the methyl esters produced is impractical and ICP–AES is the preferred method for quantitation. In this case, GC–MS can be used to confirm the identity of the product used. The analysis of occupational hygiene samples (cotton pads, gloves and socks as well as Tenax tubes and GF/A filters) spiked with metal carboxylates is demonstrated. Recoveries around 70–90% and reproducibilities of 5–23% (n=6–8) were typically achieved for the determination of tin octoate (a surrogate for zinc octoate) at spiking levels ranging from 4 to 190 μg per sampling device. Recoveries around 102–106% and reproducibilities of 10–12% (n=5–6) were typically achieved for acypetacs zinc at spiking levels ranging from 100 mg per sampling device. Reaction yields for the octoate methylation reaction were in the region of 85–87%. The method was used to monitor for occupational exposure to zinc octoate and acypetacs zinc during the application of wood treatments to fences.

Keywords: Acypetacs zinc; Zinc octoate; Pesticides

1. Introduction

Zinc 2-ethylhexanoate (commonly called zinc octoate) and acypetacs zinc are widely used active ingredients in wood preservatives and to a lesser

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extent in surface biocides. They are effective against fungi, and are often co-formulated with other active ingredients such as permethrin to broaden the range of effective protection. Additionally, zinc octoate and other metal octoates have uses in the paint and polymer industries where they are utilised as pigment dispersants, paint driers and polymerisation catalysts [1–4].

Zinc octoate is a single compound, whereas acypetacs zinc is a metal salt of complex mixtures of C8 to C10 linear and branched chain saturated carboxylic acids [5]. The branched chain acids of acypetacs are a mixture of approximately equal parts by mass of: (i) acids in which the main chain is dialkyl substituted on the second carbon atom and (ii) acids in which the second carbon atom is either unsubstituted or monoalkyl substituted. Both (i) and (ii) acids may be further alkyl substituted on the third or higher carbon atoms.

The Health and Safety Executive (HSE) regularly carries out surveys to assess the occupational exposure of workers and consumers to pesticides under normal use conditions [6–9]. Exposure surveys are conducted following recommended procedures [10–12], employing a number of sampling devices, which include cotton pads (100 cm^2) positioned on the clothing of the operator, cotton gloves and socks worn under protective gloves and shoes, and a pumped GF/A/Tenax sampler (a glass fibre filter backed up with a Tenax filled glass tube). Chemical analysis of the devices, following the pesticide treatment operation, enables calculation of the dermal and respirable exposure of the operator to the pesticide. A recent survey, investigating operator exposure during the application of amateur use pesticides, required the development of reliable methods for zinc octoate and acypetacs zinc.

There are many derivatization methods available which enable the gas chromatographic determination of acids and their salts [13]. More specifically, several methods have been reported in the literature for the determination of metal octoates [14], caprylates [15] and 2-ethyl hexanoic acid [16–18]. The most popular approaches involve derivatization of the acid or carboxylates to their pentafluorobenzyl esters [15,16], methyl esters [18] or through silylation [18], prior to gas chromatographic analysis.

This paper describes the development of a new procedure for the determination of zinc octoate and acypetacs zinc residues in occupational hygiene samples, employing an alternative methylation procedure which had been previously applied to the analysis of fatty acids [19] and phenoxy acid herbicides [20,21]. The solvent extracted analytes are converted to free carboxylic acids by partitioning with HCl, then derivatized to their methyl ester derivatives, employing trimethylsilyldiazomethane, then quantitatively (octoate) or qualitatively (acypetacs) analysed by gas chromatography with mass selective detection (GC–MS). Acypetacs zinc was determined by quantifying the zinc content of the HCl extract using inductively coupled plasma atomic emission spectroscopy (ICP–AES). GC–MS was required in order to determine the analytes in the presence of the complex hydrocarbon base solvent which is present in the formulated products. Atomic absorption spectroscopy may be a suitable alternative to ICP–AES.

Due to the non-availability of a pure standard, method development (spiked recovery) experiments were carried out using tin octoate as a surrogate reference material for zinc octoate. No such pure surrogate exists for acypetacs zinc, and hence recovery experiments were performed using a commercially purchased formulation following determination of its zinc content. Application of the method is demonstrated with the analysis of samples for zinc carboxylates collected during a survey investigating the occupational exposure to pesticides during amateur fence painting operations [6].

2. Experimental

2.1. Chemicals and solutions

2-Ethylhexanoic acid, tin(II) salt (tin octoate), 2-ethylhexanoyl chloride, methyl octanoate, trimethylsilyldiazomethane (2.0 *M* solution in hexane), dichlorodimethylsilane (99%) and hydrochloric acid (37%, 99.999%), were obtained from Aldrich UK. All solvents were Distol (pesticide residue) grade and were obtained from Fisher Scientific, UK. Methyl 2-ethylhexanoate (methyl octoate) could not be obtained from a commercial source and was synthesised from 2-ethylhexanoyl chloride, as de-

tailed later in this paper. A solution of zinc at a concentration of 1000 μg/ml in 1% w/w hydrochloric acid was purchased from Aldrich UK. Ronseal Wood Preservative (listed as 9.1% w/w zinc octoate) and Cuprinol Garden Fence & Shed Preserver (listed as 10% w/w acypetacs zinc), the products applied during the survey, were purchased from DIY retailers.

Six calibration standards of methyl octoate were prepared gravimetrically in cyclohexane to give concentrations in the range 0.1–20 μg/ml. A standard spiking solution of tin octoate was gravimetrically prepared at 145.3 μg/ml in cyclohexane. All solutions were stored in the dark at 2–8°C.

Four calibration standards of zinc and a calibration blank were prepared in 1 *M* HCl to give concentrations in the range 0.5–5 μg/ml. Cuprinol Garden Fence & Shed Preserver [stated to contain 10% w/w acypetacs zinc (or 85 g/l) equivalent to 2% w/w zinc (or 17 g/l)] was found to contain 1.83% w/w zinc (or 15.6 g/l) by ICP–AES analysis. This was used as the standard spiking solution of acypetacs zinc.

2.2. Synthesis of methyl octoate

Fifty ml (1.24 mol) of methanol was added cautiously down a reflux condenser into a 250-ml round bottomed flask containing 10 g (61.5 mmol) of 2-ethylhexanoyl chloride. The mixture was refluxed for 1 h and the excess methanol was removed by rotary evaporation to leave 6.74 g (69%) of methyl octoate which was a clear liquid. GC–MS analysis of the headspace (25 μl, collected by syringe) from above the product showed only methyl octoate (methyl 2-ethylhexanoate) to be present. This result was checked by performing GC–MS headspace analysis of the other possible contaminants, i.e. 2-ethylhexanoyl chloride, methanol and 2-ethyl hexanoic acid. The analysis results confirmed that the methyl ester product was indeed free from contaminants. Computer mass spectral library searching confirmed the identity of the methyl octoate product.

2.3. Instrumentation and apparatus

Cotton pads (Phillip Harris Medical, UK), cotton gloves (RS Electrical Components, UK), GF/A filters (Whatmans, UK) and Tenax tubes (SKC, UK) were employed for all laboratory and field experiments.

Teflon bottles of varying sizes, 30–500 ml, were obtained from Fisher Scientific UK. Ten ml Reacti-Vials with teflon/silicone backed screw caps were supplied by Pierce & Warriner UK.

All glassware was deactivated by rinsing thoroughly with a 5% solution of dichlorodimethylsilane in cyclohexane. The glassware was then rinsed three times in cyclohexane and washed (end-capped) with methanol.

A TurboVap solvent evaporator (Zymark, UK) was employed for sample concentration, where required.

Two GC–MSD systems were utilised in the study. Both consisted of a Hewlett-Packard 5890 Series II gas chromatograph fitted with a Hewlett-Packard HP-5 MS column (cross linked 5% phenyl silicone, 30 m×0.25 mm×0.25 μm film thickness). One GC was interfaced to a Hewlett-Packard 5970 Series mass selective detector, the other to a Hewlett-Packard 5972 Series mass selective detector. Both systems were controlled by Hewlett-Packard G1034C MS ChemStation software. The injection (splitless) and transfer line temperatures were 250 and 280°C, respectively, and the oven temperature programme was 60°C for 1 min, ramping at 20°C/min to 300°C and holding for 1 min. Total run time is 14 min. Helium (>99.996%) was used as the carrier gas and electronic pressure control in constant flow mode delivered 0.98 ml/min. Selected Ion Monitoring (SIM) data was collected between 3.5 and 5.5 min, monitoring ions with m/z=87, 102 and 130, for methyl octoate. Scan data was obtained for the qualitative analysis of acypetacs methyl, but SIM analysis could be used at lower levels, monitoring ions with m/z=74, 101 and 102 which are representative of fragment ions observed for branched C8 and C9 methyl esters present in acypetacs (74=$[C_3H_6O_2]^{+\cdot}$, 101=$[C_5H_9O_2]^{+}$ and 102=$[C_5H_{10}O_2]^{+\cdot}$).

A Perkin-Elmer Optima 3000DV ICP–AES equipped with a Perkin-Elmer AS 91 autosampler was utilised throughout the study. The ICP–AES was operated in radial viewing mode with a radio frequency (RF) generator power of 1300 W and nebuliser and plasma gas flow-rates of 0.80 and 15

l/min, respectively. Emission wavelengths of 213.856 and 202.548 nm were monitored.

2.4. Procedures

Fig. 1 presents schematically the process of extraction and analysis of the organo-zinc based fungicides.

2.4.1. Spiked samples

For tin octoate, the sampling devices were spiked by syringe, with various volumes of the standard spiking solution. Spiking levels were: 250 μl added to pads to give 36.3 μg spiked; 625 μl added to gloves to give 90.8 μg spiked; 1300 μl added to socks to give 188.9 μg spiked; 25 μl added to GF/A filters to give 3.63 μg spiked; 25 μl added to Tenax sorbent to give 3.63 μg spiked. The spiked samples were left for 2 h at room temperature to allow the solvent to evaporate.

For acypetacs zinc, 1 ml of Cuprinol Garden Fence & Shed Preserver was added to pad, glove and sock devices producing a spike equivalent to 78 mg of acypetacs zinc (i.e. 15.6 mg of zinc and 62.4 mg of acypetacs) per device. Additionally, controls were assessed whereby clean, empty, 30 ml Teflon bottles were spiked with 1 ml of sample. The spiked samples were left for 2 h at room temperature to allow solvent to evaporate. GF/A filters and Tenax sorbent were not assessed for this analyte.

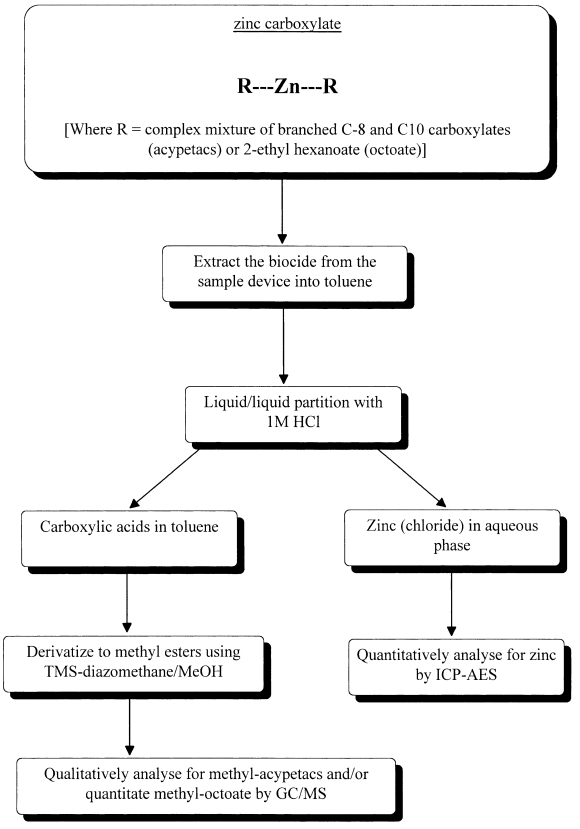

Fig. 1. Quantitative and qualitative analysis of occupational hygiene sampling devices exposed to zinc carboxylate containing timber treatments.

2.4.2. Field samples

Field samples were exposed during amateur application of timber treatments and were collected following standard occupational exposure survey protocol [10–12]. The samples were stored frozen in individual plastic bags prior to extraction, derivatization and analysis.

2.4.3. Extraction

All devices were placed into Teflon bottles and toluene was added to extract the pesticide. Pads and controls were extracted with 20 ml, gloves with 50 ml, socks with 200 ml, and GF/A and Tenax 2 ml. The bottles were sealed then placed in an ultrasonic bath for 1 h.

2.4.4. Concentration

In order to improve sensitivity, some of the zinc/tin octoate extracts were concentrated using the Zymark TurboVap sample evaporator, prior to acid partitioning. Ten ml of pad extracts and 20 ml of the glove and the sock extracts were concentrated to 1 ml.

2.4.5. Acid partitioning

Portions of the extracts, were removed from the bottles and placed into Reacti-Vials. Four ml was collected for the acypetacs zinc exposed samples and 1 ml for the concentrated zinc/tin octoate samples (2 ml for GF/A and Tenax). One ml of 1 *M* HCl was added and the Reacti-Vials were shaken vigorously for 2 min and allowed to separate into two layers. The acid phase was removed from the vials by Pasteur pipette prior to ICP–AES analysis to de-

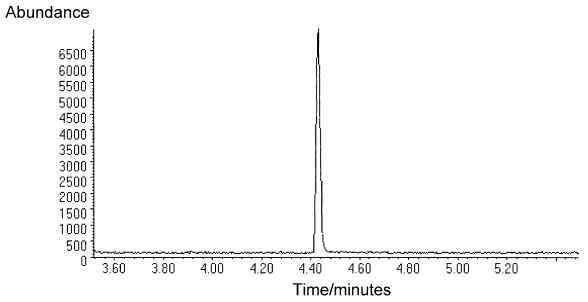

Fig. 2. GC–MSD selected ion chromatogram for methyl octoate *m/z* 102 for a real sample (i.e. left hand glove), showing the effectiveness of SIM in resolving the analyte from the matrix.

termine the zinc content (acypetacs zinc only). Then, 0.5 ml of the acid extracts from the spiked samples had to be diluted prior to analysis, to give an effective (standardised) 100 ml volume relative to the spike (i.e. dilutions of 1:20 were used for pads, 1:8 for gloves and 1:2 for the socks). Acid extracts from field samples were analysed directly.

The remaining toluene layer was dried using sodium sulphate prior to derivatization.

2.4.6. Derivatization

Aliquots of the dried toluene extracts (2 ml for pads, gloves, socks and controls, and 1 ml for Tenax and GF/A) were placed into clean Reacti-Vials. Methanol (450 μl for pads, gloves, socks and controls, and 225 μl for Tenax and GF/A) was added along with trimethylsilyldiazomethane (2.0 *M*), 50 μl for pads, gloves, socks and controls, and 25 μl for Tenax and GF/A. The total volumes were 2.5 ml for pads, gloves, socks and controls, and 1.25 ml for Tenax and GF/A giving a dilution factor of 1.25 for all devices. The Reacti-Vials were capped and sonicated for 30 min. The solutions were then transferred to GC vials for analysis of methyl ester contents by GC–MS.

3. Results and discussion

3.1. Tin and zinc octoates

Fig. 2 shows the selected ion chromatogram (SIC) results for the methyl octoate derivative in a glove field sample which was found to contain 176 μg of zinc octoate. The chromatogram shows that the methyl octoate peak is well resolved from interferences which are probably co-extracts from the pad and glove sampling devices. All calibration graphs were linear (correlation coefficients of 1.000) over the standard range i.e. 0.1–20 μg/ml.

The results of the spiking experiments are presented in Table 1. The mean recoveries, around 70–90%, are within what are generally considered acceptable limits, i.e. 70–110%. The lowest result was obtained for the GF/A filters which may be due to the active sites found on these devices. This proposal is supported by the fact that the highest recovery is obtained for the inactive Tenax sorbent. The estimated limits of detection (3×signal/noise), which range from 5 to 460 ng/device, are adequate for determining the levels of exposure typically experienced [6–9]. Analysis of blank samples revealed no trace of the pesticide.

The reaction yield for the derivatization step was determined using tin octoate due to the non-availability of a pure standard of zinc octoate. This was found to be around 85–87% which, although lower than would be desired, is more than acceptable. There is no reason to expect that the reaction yield for the derivatization of the zinc octoate would be sig-

Table 1
Tin octoate recovery data (determined as methyl octoate) from spiking experiments on occupational hygiene devices

Device	Number of replicates	Theoretical content (μg/device)	Mean analysis result (μg/device)	2× SD	% Recovery ±2× SD	Limit of detection[a] (ng/device)
Pad	8	36.3	27.0	4.3	74.5±15.8	46
Glove	6	90.8	66.2	9.0	72.9±13.6	138
Socks	6	188.9	154.3	35.2	81.7±22.8	460
Tenax	6	3.63	3.24	0.16	89.3±5.0	5
GF/A filter	6	3.63	2.51	0.24	69.2±9.6	5

[a] All limits of detection were determined on the 5972 series MSD.

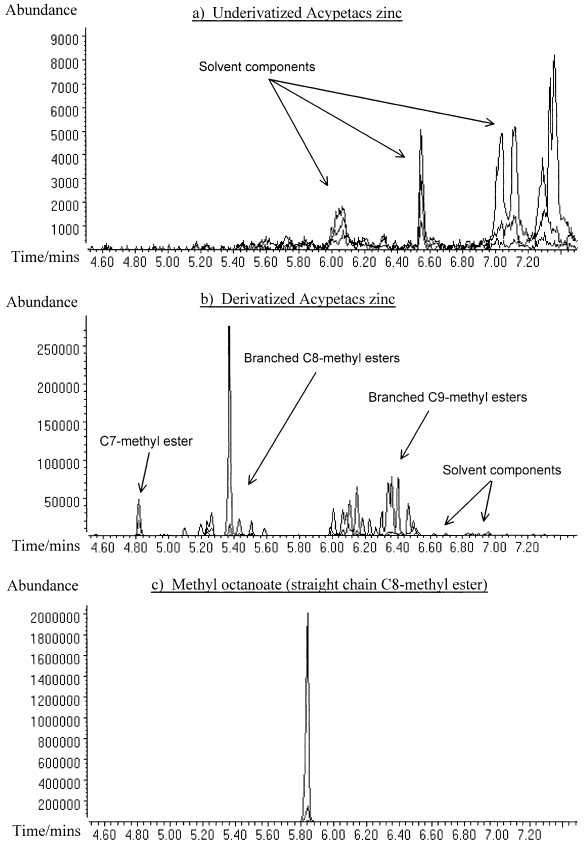

Fig. 3. Qualitative GC–MS (selected ion chromatograms: m/z= 74, 101 and 102) analysis of acypetacs zinc extracts.

nificantly different to that of tin octoate. The reaction yield may explain the somewhat low overall recoveries achieved in the spiking experiments (i.e. recovery result=recovery+reaction yield). Therefore, recovery correction must be applied to any results obtained using this method.

The derivatization reaction utilising trimethylsilyldiazomethane, offers significant benefits over other reported methods in that a safe and efficient reaction is employed under mild conditions. This reaction would not be limited to the determination of tin and zinc octoates in occupational hygiene samples but should be applicable for many more sample types, including environmental matrices, providing the analytes can be extracted into toluene.

3.2. Acypetacs zinc

Fig. 3 shows SIC results (m/z 74, 101 and 102) for the same acypetacs zinc extract following acid partitioning, (a) underivatized and (b) derivatized. This example clearly illustrates that derivatization is required in order to derive any qualitative information on the carboxylate species present. This could be of use, for example, in determining if a product contained zinc octoate, zinc naphthenate or acypetacs zinc. Identification of the peaks as either C7, C8 or C9 was established from the highest mass ions observed in the mass spectra ($[M–H^{\cdot}]^{+}=m/z$ 143, 157 and 171, respectively) and by comparison with the retention time for methyl octanoate. Methyl octanoate being unbranched would be expected to have a longer retention time than its branched C8 methyl ester analogues and this is observed in Fig. 3c). The average chain length for acypetacs was estimated to be C8.5. Unfortunately the complex nature of the products obtained prevents quantitative GC–MS from being performed.

ICP–AES was used to produce quantitative data on the zinc content of the acid extract. The recovery results for the zinc analyses are presented in Table 2. The recoveries which range from 102 to 106% are within what are generally considered acceptable limits, i.e. 70–110%. The estimated limits of detection (3×signal/noise), which range from 4 to 40 ng/device (assuming that sample extracts undergo a 10-fold concentration and that a 1:1 solvent–acid partition is used) are adequate for determining the

Table 2
Zinc recovery data from acypetacs zinc spiking experiments on occupational hygiene devices

Device	Number of replicates	Theoretical zinc content (mg/device)	Mean analysis result: zinc content (mg/device)	2× SD	% Recovery ±2× SD	Limit of detection (ng/device)
Control	11	15.6	14.2	3.0	91±21	N/A
Pad	6	15.6	15.5	1.6	99±10	4
Glove	6	15.6	15.0	1.6	96±11	20
Sock	5	15.6	14.8	1.8	95±12	40

levels of exposure typically experienced [6–9]. Analysis of blank samples revealed no trace of the pesticide. All calibration graphs were linear, with a correlation coefficient of 0.9999 or better, over the standard range, i.e. 0–5 μg/ml.

Conversion of zinc to acypetacs zinc results was performed, assuming the average acypetacs chain length to be C8.5. The acypetacs zinc in this case would have an average molecular mass of 365 Daltons, with a zinc content of 17.8%. This is consistent with the analysis result for the bulk formulation where we detected 1.83% zinc in a stated content of 10% acypetacs zinc (i.e. the zinc content of zinc octoate was determined at 18.3%). Thus zinc results were converted to acypetacs zinc through a multiplication factor of 5.56.

3.3. Analysis of field samples

Table 3 presents the data obtained from the analysis of survey samples exposed to organo-zinc compounds, employing the methods described in this paper. The exposure data derived is consistent with data obtained for the other analytes which were applied during this study [6]. The acypetacs zinc values detailed in Table 3 have been determined from the zinc results using the conversion factor described in the previous section.

4. Conclusions

The method described in this paper provides a simple route for the determination of both tin and zinc octoates and acypetacs zinc from occupational hygiene samples.

The acid partitioning step has been shown to be an efficient way to isolate the metal and organic acid components prior to analysis by two different analytical techniques.

Trimethylsilyldiazomethane is an effective reagent for the methylation of the extracted carboxylic acids and a safer alternative to diazomethane. Subsequent GC–MSD (SIM) analysis of the organic extract following derivatization can be used to quantify and/or identify the resultant methyl esters. Good recoveries have been achieved reproducibly for metal octoates and the limits of detection are acceptable for the residue analysis required to determine occupational exposure. ICP–AES analysis of the acid extracted zinc has been shown to provide similarly good quantitative results, but this route would re-

Table 3
Analysis results for field samples collected during survey of amateur exposure to fence painting biocides

Sample type	Location	Results [μg/device (unless stated)]	
		Zinc octoate	Acypetacs zinc
Bulk (% w/w)		9.6 (9.1)[a]	10.1 (10)[a]
GF/A	Breathing zone	5	83
Tenax	Breathing zone	NQ	ND
Pad	Head	1 mg/device	11
Pad	Chest (outer)	344	17
Pad	Chest/ankle[b] (inner)	9	11
Pad	Right wrist	4.6 mg/device	6
Pad	Left thigh	538	17
Pad	Left ankle	524	17
Pad	Back	611	6
Glove	Right hand	803	65 mg/device
Glove	Left hand	176	150
Sock	Right foot	NQ	50
Sock	Left foot	137	44

ND, not detected; NQ, detected but not quantified (below calibration range).
[a] Stated content.
[b] Different positions were used to assess clothing penetration; chest for zinc octoate, ankle for acypetacs zinc.

quire qualitative GC–MS analysis if speciation (identification) is needed.

It is expected that the method described here would be applicable to many more acid based organo-metallic species and could be extended to include a wider range of samples, such as environmental samples and bulk formulations.

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