Development of Automated Headspace Gas Chromatography Determination of Dithiocarbamates in Plant Matrixes

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The determination of dithiocarbamates in plant matrixes is generally carried out by spectrophotometric (European Norm EN 12396-1, 1996) or gas chromatography headspace (European Norm EN 12396-2, 1999) methods. However, the former method presents a risk of carbon disulfide loss during hydrolysis and distillation and its sensitivity is low, whereas the latter method is time-consuming. In comparison to these European methods and in compliance with norm V03-110, we have developed an automated gas chromatography headspace method. This method offers a good level of accuracy and precision and is specific to the compound determined (CS_2). The limit of detection is below 0.020 mg/kg and the limit of quantification is below 0.050 mg/kg. Moreover, the recovery rates are between 85 and 103% with RSD less than 20%. The automated headspace method has several advantages when compared to the spectrophotometric and manual headspace methods, including the reduction of reagents employed for extraction and a greater number of analyses achievable per day than the other methods (≈40 samples of food).

Keywords: *Dithiocarbamates; automated headspace gas chromatography; plant matrixes; fungicides*

INTRODUCTION

Many fungicides used in agriculture are metal salts containing manganese (maneb), iron (ferbam), zinc (zineb, mancozeb, propineb), or sodium (metiram). These dithiocarbamates are used for the treatment of about 400 pathogens on more than 70 cultures (potato, lettuce, blackcurrant, onion, etc.). Dithiocarbamates present a low toxicity, but the metabolites and degradation products of bisdithiocarbamates, ethylene thiourea or propylene thiourea, affect the thyroid, and furthermore, neurotoxic effects have also been observed. Because of their chelating properties, dithiocarbamates inhibit enzymes containing Fe, Cu, Zn, or thiol groups.

Until now, the determination of dithiocarbamates was carried out using the spectrophotometric method (*1*, *2*) by measuring CS_2 produced during acidic hydrolysis. To determine more specifically dithiocarbamates, numerous different methods were developed, such as UV spectroscopy for quantitating isothiocyanates (R−N═C═S) and dithiocarbamates (*3*). In the same way, determination of ferbam (ferric dimethyldithiocarbamate) was performed by capillary electrophoretic methods with UV detection (*4*) or with diode array detection (*5*). Determination of dithiocarbamates was also carried out by amperometric biosensor (*6*, *7*). Other methods for the determination of dithiocarbamates were developed, including adsorptive stripping voltametry (*8*) and Raman and surface-enhanced Raman spectroscopy (*9*). Analysis could be carried out by reversed-phase liquid chromatography after formation of metal ion complexes (*10*). Chromatographic analyses were performed to determine dithiocarbamates by measuring amounts of ethylenethiourea formed after extraction from food samples and cleaned up by a combination of two-step derivatization and liquid−liquid partition. The detection of derivatized product was carried out by ECD or NPD (*11*).

Unfortunately, these methods present a risk of carbon disulfide loss during hydrolysis and distillation, and they are time-consuming, require many reagents, and have a low sensitivity (the limit of detection of the spectrophotometric method is only 0.2 mg/kg). Moreover, these methods suffer from interference of various ions and the possibility of finding false positive samples. Furthermore, to reach a limit of quantification in dithiocarbamates, expressed in CS_2, in plants compatible with the lowest maximal residue limits (0.050 mg/kg for blackcurrants and potatoes), and because spectrophotometric methods could not satisfy these criteria, it was necessary to develop new technology for the determination of dithiocarbamates. Recently, an alternative spectrophotometric method was used to determine dithiocarbamates (*12*). Carbon disulfide liberated during hydrolysis is absorbed in ethanolic sodium hydroxide solution to form xanthate. The xanthate is subsequently treated with potassium iodate and *N*-chlorosuccinimide to liberate free iodine. Crystal violet dye was formed through selective oxidation of leucocrystal violet by liberated iodine, which has an absorbance at 595 nm. Although this method is sensitive, it does not solve the problem of the loss of CS_2 during the process. Finally, a European method was drawn up, using a manual headspace method for the determination of dithiocarbamates (*13*), but this method is time-consuming.

In the present communication, a simple, sensitive, and rapid method, consisting of the miniaturization and automatization of the headspace, for the determination

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10.1021/jf0013196 CCC: $20.00
Published on Web 04/20/2001

of dithiocarbamates was developed and validated against norm V03-110 (*14*).

EXPERIMENTAL PROCEDURES

Safety. Because of the toxicity of the reagents, the sample preparation procedure should be performed in a well-ventilated hood, and the analyst should wear protective gloves.

Instrumentation. Spectrophotometric analyses were carried out on a Lambda 20 Perkin-Elmer spectrometer at 435 nm, using 1-cm quartz cells.

Gas chromatographic analyses were carried out on a Varian model 3800 gas chromatograph (Walnut Creek, CA) fitted with a 1079 injector, a septum programmable injector (SPI) inlet, and an electron capture detector. Injections were made manually or with a CombiPal autosampler (CTC Analytics). Operating temperatures of the injector and the detector were 200 °C and 300 °C, respectively. Chromatographic separation was performed with a 30 m × 0.53 mm i.d. DB-WAX (Varian Instruments) fused-silica capillary column coated with a 1-μm thickness of poly(ethylene glycol) film. Nitrogen 5.0 was used as carrier gas with constant pressure (3 psi). The initial column temperature was 30 °C (hold 7 min.) and was raised at a rate of 20 °C/min to 220 °C (hold 7 min.).

Reagents, Solutions, and Glassware. A standard sample of mancozeb of 85.6% purity was obtained from Elf Atochem, thiram of 99.0% purity came from Cil Cluzeau, natriumdiethyldithiocarbamat trihydrate (DEDTC) of 99.1% purity was obtained from Riedel-de Haen, and carbon disulfide of 99.9% purity came from Merck. Methanol, ethanol, hydrochloric acid 37%, and sodium hydroxide were purchased from Merck. Copper II acetate was bought from Prolabo, and diethanolamine was purchased from Sigma-Aldrich. Lead II acetate trihydrate and tin II chloride dihydrate were purchased from Acros. All reagents were analytical grade, and ultrapure water obtained by ultra filtration (Seral System) was used for experiments.

Stock solutions of lead acetate (300 g/L), NaOH (100 g/L), copper II acetate (0.4 g/L), and diethanolamine (100 g/L) were prepared in ultrapure water.

A colored reagent solution was prepared in a 250-mL flask (30 mL of copper II acetate solution and 35 g of diethanolamine) made up to 250 mL with ethanol. Two solutions of tin II chloride/hydrochloric acid were prepared. Solution 1 (used for spectrophotometric method) was 20 mL of tin II chloride solution (400 g/L of $SnCl_2$ in concentrated hydrochloric acid), 20 mL of concentrated hydrochloric acid made up to 200 mL with ultrapure water. Solution 2 (used for manual and automated headspace methods) was 640 mL of concentrated hydrochloric acid and 36 g of tin II chloride made up to 1000 mL with ultrapure water. Solution 2 was boiled for 30 min prior to use.

Carbon Disulfide Solutions. Each day of analysis, a carbon disulfide solution was prepared. A 50-mL flask containing 40 mL of ethanol was weighed; 1 mL of carbon disulfide (purity 99.9%) was added and the flask was again weighed. The quantity of carbon disulfide was precisely noted. The volume of ethanol was adjusted to have a stock solution of 50 mL, which was diluted to 1/500 (daughter solution of CS_2).

DEDTC, Thiram, and Mancozeb Solutions. Natriumdiethyldithiocarbamat trihydrate (DEDTC), thiram, and mancozeb stock fortifying solutions were separately prepared by dissolving a known amount of each analyte in ultrapure water to obtain a stock solution of exactly 100 mg/L carbon disulfide equivalent. A 10-mL portion of stock solution was taken with precision and diluted in a volumetric flask (100 mL) to obtain a working fortifying solution at 10 mg/L carbon disulfide equivalent.

Spectrophotometric Method. Samples of vegetable matrixes were heated with a solution of tin II chloride and hydrochloric acid to form carbon disulfide which was distilled and collected in an ethanolic solution of cupric acetate and diethanolamine. Two yellow cupric-*N*,*N*-bis(2-hydrxy-ethyl) dithiocarbamate complexes with molar ratios of Cu/CS_2 1:1 and 1:2, respectively, were formed and were measured jointly by spectrometry.

Preparation of the Apparatus. In the first bubbler, 10 mL of lead II acetate solution was added; 10 mL of hydroxide solution was adding in the second; and 15 mL of colored reagent solution was placed in the third and the fourth. The bubblers were connected by spherical socket joints (the first being attached to the condenser), all joints had to be absolutely gastight. A gas inlet tube was inserted to the bottom of the flask and was opened to have an air intake through the flask. A water-flow was turned on through the reflux condenser and the water jet pump was turned on in order to create a weak vacuum, to pull air through the four bubblers. The air flow rate was approximately three to five bubbles of air per second passing through the system.

Decomposition and Distillation. In a three-necked flask of 1 L, 20 g of matrix and the 200 mL of solution 1 were added. The three-necked flask was rapidly connected to the first bubbler and the solution was rapidly brought to the boil and was maintained at boiling point for 1 h. At the end of this period, the bubblers were disconnected and the air flow was turned off. The contents of the first and the second bubblers were discarded, and the content of the third bubbler was transferred into a 25-mL flask and made up to 25 mL with ethanol. In the case of samples containing a high concentration of dithiocarbamates, the colored reagent of the third bubbler was saturated and a coloration appeared in the fourth bubbler. In this case, the contents of these two bubblers were transferred into a 50-mL flask and made up to 50 mL with ethanol.

Spectrophotometric Measurements. The measurements were carried out in the spectrophotometer at 435 nm, using 1-cm quartz cells. An auto zero point was made using the colored reagent (15 mL of the colored reagent made up to 25 mL with ethanol). From the daughter solution of carbon disulfide, solutions at 0.2, 0.5, 0.8, 1.0, 2.0, and 3.0 mg/L carbon disulfide equivalent were freshly prepared each day in 25-mL flasks. In each flask, 15 mL of colored solution made up to 25 mL with ethanol was added.

Headspace Method. *Manual Method.* Standard solutions of DEDTC (0.030, 0.050, 0.100, 0.200, 0.500, and 1 mg/kg CS_2 equiv) were prepared in ultrapure water made up to 20 mL with ultrapure water. In a 250-mL round-bottomed flask (previously warmed in a dry oven at 65 °C) 20 g of matrix or the 20 mL of standard solution, 56 mL of tin II chloride/hydrochloric acid solution (solution 2), and 37.5 mL of diethanolamine solution were added. (Before use, these solutions were heated and maintained at 90 °C in a water-bath.) The reaction flasks were immediately capped with a silicone septum cap and were heated and maintained at 90 °C for 1 h with periodic manual agitation. At the end of the reaction, 200 μL of gas was taken and injected into a gas chromatograph with a gas syringe warmed at 50 °C in a dry oven.

Automated Method. Standard solutions (0.010, 0.025, 0.050, 0.100, 0.200, and 0.500 mg/kg of CS_2 equivalent) were prepared in ultrapure water. In a 20-mL vial, 2 g of matrix or 2 mL of standard solution, 6 mL of tin II chloride/hydrochloric acid solution (solution 2), and 4 mL of diethanolamine solution were added. These solutions were introduced at room temperature. The vials were immediately crimped and were placed in the tray. The Combi Pal system took a vial from the tray and placed it in the incubator where it was heated at 90 °C during 30 min. The vial was agitated for 99 s with an agitation speed of 500 rpm and was kept in repose for an additional 99 s after agitation. At the end of the incubation period, the Combi Pal took 200 μL with a gas syringe maintained at 50 °C and this volume of gas was directly injected into the gas injector port. The filling speed was 20 μL per second, the pull up delay was 1 s, the injection speed was 100 μL per second, the preinjection delay was 0.5 s, and the postinjection delay was 5 s. After each injection, the syringe was cleaned with nitrogen in a backflush system for 20 s.

Fortification. Vegetable samples were fortified with the appropriate working calibration solution of DEDTC to produce fortification levels of 0.05−0.5 mg/kg, measured in CS_2 equivalent.

Table 1. Recovery Rates Obtained on Untreated Lettuce (25 g) Spiked at 10 mg/kg with Mancozeb, Thiram, and DEDTC[a]

dithiocarbamate	recovery rate (%)
Mancozeb	80.4
Thiram	92.0
DEDTC	85.6

[a] Measurements were made by spectrophotometric method.

Crushing. Vegetable samples were crushed frozen using a food processor with stick dry ice until complete homogenization of the samples.

RESULTS AND DISCUSSION

The methods are based on the decomposition of dithiocarbamates in acidic conditions to release carbon disulfide (CS_2) derived from dithiocarbamates. The diethanolamine solution enhances the solubility of dithiocarbamates in the medium, and the metal ion used in the acidic hydrolysis participates in cleavage of the S−S bond and immediate decomposition to CS_2 in acidic solution. It prevents or greatly retards an alternate pathway that yields ethylene thiourea, rather than carbon disulfide, as a stable product. In the spectrophotometric method, lead acetate scavenges hydrogen sulfide in the first bubbler (*15*). In the chromatographic method, the temperature program used enables the correct separation of the air peak and CS_2 peak (Figure 1). The retention time of CS_2 is approximately 2 min.

To validate the use of DEDTC, recovery rates were determined on lettuce spiked with mancozeb, thiram, and DEDTC at 10 mg/kg (CS_2 equivalent) and analyses were made using the spectrophotometer method. In this case, at the end of hydrolysis, the contents of the two last bubblers were transferred into a 50-mL flask and made up to 50 mL with ethanol. This experiment made it possible to see if a high concentration of carbon disulfide does not saturate the fourth bubbler. Results obtained showed that yields were between 80.4 and 92.0%, whatever the standard used, when DEDTC was used for experiments (Table 1). As a consequence of this observation, samples were spiked with DEDTC.

Generally, the determination of dithiocarbamates was made with fresh vegetable matrixes because it was demonstrated that crushing led to the demolition of dithiocarbamates. As a consequence, the effect of crushing was studied. Samples of lettuce, blackcurrant, and onion, naturally treated with dithiocarbamates, were analyzed. Five extractions for lettuce and blackcurrant and three extractions for onion were made, noncrushed and crushed, using the spectrophotometric and the manual headspace methods (Table 2). Concentrations of carbon disulfide obtained with the spectrophotometric method were 11.9 mg/kg for crushed and noncrushed lettuce with relative standard deviation (RSD) about 15%. For blackcurrant, concentrations were 0.50 and 0.56 mg/kg with RSD about 20% for noncrushed and crushed samples; and for onion, concentrations were 0.47 and 0.46 mg/kg with RSD about 5%. With the manual headspace method, concentrations were 12.5 and 11.7 mg/kg for crushed and noncrushed lettuce with relative standard deviations equal to 5.8 and 18.6%, respectively. For blackcurrant, concentrations were 0.55 and 0.68 mg/kg with RSD equal to 19.8 and 49.5%, respectively, for crushed and noncrushed samples; and concentrations were 0.37 mg/kg with RSD equal to 15% for onion.

Table 2. Concentrations and Relative Standard Deviations Obtained on Non-Crushed and Crushed Vegetable Samples by Spectrophotometric Method and Manual Headspace Injections (results are expressed in mg of CS_2/kg)

		spectrophotometric		manual	
vegetable		non-crushed	crushed	non-crushed	crushed
lettuce ($n = 5$)	mean	11.9	11.9	11.7	12.5
	RSD	16.5	15.0	18.6	5.8
blackcurrant ($n = 5$)	mean	0.50	0.56	0.68	0.55
	RSD	20.0	20.4	49.5	19.8
onion ($n = 3$)	mean	0.47	0.46		0.37
	RSD	6.0	3.3		15.0

Table 3. Reproductibility and Linearity in the Quantification of Various Amounts of CS_2 Obtained from Model Solutions by Manual and Automated Headspace Injections

	manual			automated	
	arbitrary units ($n = 5$)			arbitrary units ($n = 5$)	
CS_2 (mg/kg)	measured	decreased by 3821	RSD (%)	measured	RSD (%)
0.000	3821	0	15	0	-
0.010				1027	8
0.025				2504	5
0.030	9003	5182	7		
0.050	12502	8681	15	4829	7
0.100	17457	13636	19	8788	10
0.200	26861	23040	16	18627	13
0.500	62764	58943	20	43256	9
1.000	117068	113247	4		

The measured concentrations in CS_2 were in the same proportion, whatever the method used for extraction, and for noncrushed and crushed samples. These results have shown that crushing does not have an effect on the determination of dithiocarbamates. Moreover, RSDs were better for crushed samples with the manual headspace method but were on the same order with the spectrophotometric method, with the exception of the onion matrix. It can be assumed that, for the spectrophotometric method, the repeatability calculated is due to the process, and that the crushing does not improve results. On the other hand, when using the manual headspace method, repeatability was better when samples were crushed. Crushing produced improved results because the sample was more homogenized. Consequently, experiments were made with crushed samples.

Determination of Detection and Quantification Limits. To determine the detection and quantification limits for manual and automated headspace methods, six different concentrations of solutions were prepared. For each concentration, five solutions were prepared. In addition, a solution containing only reagents, without DEDTC, was injected in order to determine if interferences were present. The calibration curves were defined with the average chromatographic peak areas of CS_2 (Table 3 and Figure 2). Because of a better signal-to-noise ratio, the first scale point was 0.010 mg/kg in automated mode whereas it was only 0.030 mg/kg in manual mode. The relative standard deviations were better in automated mode than those in manual mode. Moreover, an interference was present when injections were made in manual mode; a peak was detected with

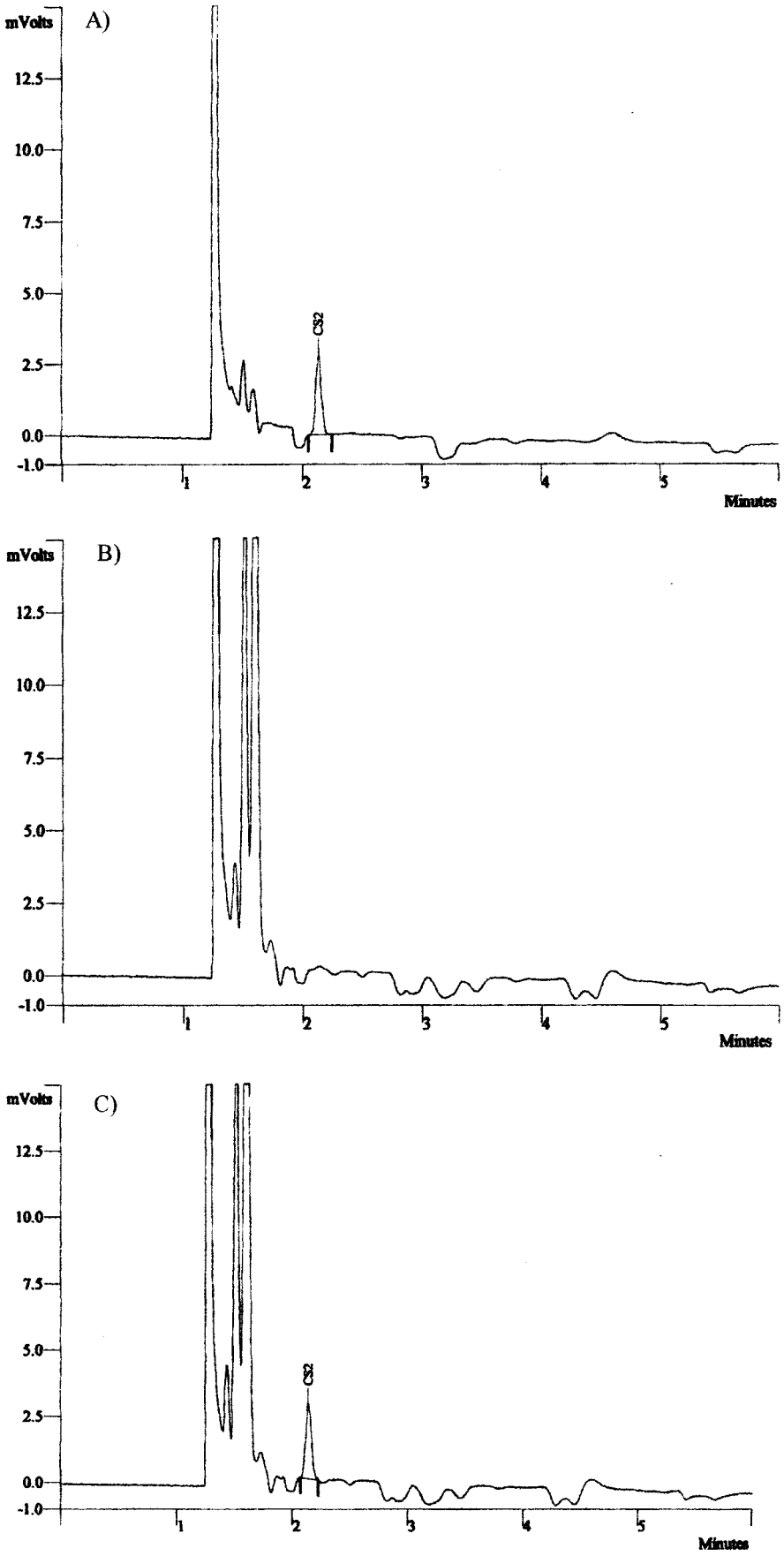

Figure 1. Chromatograms of carbon disulfide obtained by automated headspace method of (A) standard DEDTC (concentration in CS_2 = 0.100 mg/kg); (B) untreated sample of potato; and (C) untreated sample of potato spiked at 0.100 mg/kg of CS.

an area above 3000. The calibration curve for determination of detection and quantification limits was calculated with a range from 0 to 1 mg/kg for manual mode and from 0 to 0.500 mg/kg for automated mode. Equa-

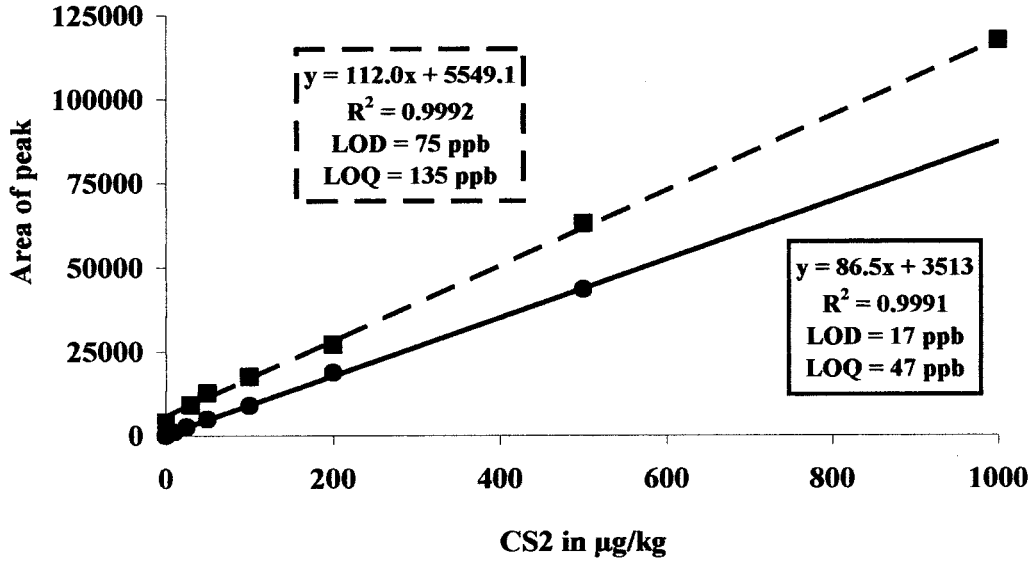

Figure 2. Calibration curves of CS_2 obtained by manual ------ and automated — headspace methods.

tions of calibration curves were equal to

$$Y = 112.0x + 5549.1 \text{ for manual mode } (r^2 = 0.9992)$$

$$Y = 86.2x + 351.3 \text{ for automated mode } (r^2 = 0.9991)$$

The two calibration curves were linear for a wide range of concentrations with a coefficient of correlation above 0.999. Results obtained made it possible to calculate the sensitivity (detector response) and the coefficient of the blank (effect of reagents). The sensitivity of the two methods, corresponding to the slope of the curves, was similar, but the ordinates of origin were very different. In the case of automated injections, the response of the reagent was no different from that of manual injection in which a response appeared. The detection limits calculated in compliance with norm V03-110 were 0.075 mg/kg and 0.017 mg/kg for manual and automated modes, respectively. The quantification limits were 0.135 mg/kg and 0.047 mg/kg.

In manual injection mode, the relative standard deviations were between 15 and 20%, except for the concentration 0.030 and 1 mg/kg (RSD < 10%). These RSDs were due not only to the preparation but also to the injection speed and to the volume of the gas taken, which were not easily repeatable. Moreover, the presence of an interference in the blank reagent contributed to a limit of quantification greater than 0.100 mg/kg. This interference could be derived from air or reagent contaminants. To reduce this problem, all reagents were boiled and glasses were silanisated before use. Six solutions and a blank were prepared and injected three times. No interference was present in the blank, and the calibration curve was recalculated. The detection and quantification limits were 0.038 mg/kg and 0.069 mg/kg, respectively. In automated mode, relative standard deviations were generally higher (below 15%); the concentrations of CS_2 at 0.100, 0.200, and 0.500 mg/kg present a higher RSD. Moreover, repeatability of injections was better in automated than in manual mode; the RSDs were essentially due to the sample preparation.

Determination of the Specificity. The specificity of the method consists of quantifying CS_2 formed after addition of DEDTC on field-treated samples. Results observed must be representative of the DEDTC added and no matrix effects must be observed. Results obtained are presented in Table 4. For manual headspace, considered as the reference method, only one extraction was carried out for each matrix; three extractions were carried out for automated headspace. Recoveries were calculated with the following equation:

$$Recovery = \left[\frac{Measured - Quantity\ of\ CS_2\ observed}{Spiking\ level}\right] \times 100$$

For manual headspace, recovery rates were between 77 and 150%, and for automated injections, recovery rates were between 80 and 128%. Moreover, relative standard deviations were less than 20% for automated injections. The slopes of the re-covering of the straight line, proportional to the quantity of CS_2 observed and the quantity of CS_2 added, are equal to 1.925 and 1.051, and the signification test (Table 7) was 1.938 and 0.627 for manual and automated injections, respectively (critical value given in the Student table is 2.571 at 5% risk level). In automated mode, the slope was practically equal to 1, which confirms that no matrix effect was present. In manual mode, this slope was equal to 1.925, due to the presence of an interference in the blank reagent. These two methods could be considered as specific.

Determination of the Precision and Accuracy. This experiment plan has made it possible to compare standard deviation (precision) and averages (accuracy) between reference and alternative methods. At first, the determination of the precision and accuracy was made for manual headspace, considered as the alternative method, in comparison to the spectrophotometric method, considered as the reference method (Table 5). To determine these parameters, several extractions were carried out with the reference and with manual headspace methods. The repeatabilities of results were of the same order for spectrophotometric and manual headspace methods (around 15−25% for spectrophotometric and 10−20% for headspace). Differences observed between these two methods have shown that concentrations calculated are not very different. To compare automated and manual injections, only one extraction was per-

Table 4. Recovery of CS_2 on Field-Treated Matrixes Spiked with DEDTC Measured by Manual and Automated Headspace Methods

	Manual Headspace			
	quantity of CS_2 observed (mg/kg)	spiking level (mg/kg in CS_2)	measured (mg/kg in CS_2)	recovery (%)
potato	0.09	0.30	0.39	100
onion 1	0.37	0.30	0.62	83
leek 1	0.67	0.50	1.42	150
leek 2	0.29	0.30	0.52	77
allium	0.08	0.10	0.06	n.d.[a]

	Automated Headspace				
	quantity of CS_2 observed (mg/kg)	spiking level (mg/kg in CS_2)	average measured (mg/kg in CS_2) ($n = 5$)	recovery (%)	RSD (%)
blackcurrant 3	0.05	0.10	0.13	80	16
blackcurrant 4	0.23	0.25	0.43	80	4
potato 2	0.03	0.02	0.05	100	2
potato 3	0.02	0.01	0.03	100	12
onion 2	0.13	0.10	0.21	80	16
onion 3	0.28	0.25	0.60	128	2

[a] n.d., not detected.

Table 5. Comparison of the Determination of Dithiocarbamate Residues in Field-Treated Matrixes by Spectrophotometric Method and Manual Headspace Injections (results are expressed in mg of CS_2/kg)

	spectrophotometric		manual		
	average (mg/kg)	RSD (%)	average (mg/kg)	RSD (%)	difference[c] (%)
lettuce[a]	11.86	15.0	11.95	10.6	0.09
blackcurrant 1[a]	0.56	20.4	0.55	19.8	−0.01
blackcurrant 2[a]	0.74	22.6	0.41	12.6	−0.33
potato[b]	0.29	13.8	0.09	22.2	−0.20
onion[b]	0.46	3.3	0.37	15.0	−0.09
leek[b]	0.92	25.1	0.67	4.8	−0.25
allium[b]	0.18	11.8	0.08	25.0	−0.09

[a] $n = 5$ extractions. [b] $n = 3$ extractions. [c] Difference: results obtained by manual headspace − results obtained by spectrophotometric method.

Table 6. Comparison of the Determination of Dithiocarbamate Residues in Field-Treated Matrixes by Manual (M) and Automated (A) Headspace Injections (results are expressed in mg of CS_2/kg)

	manual	automated ($n = 5$)		
	results (mg/kg)	average (mg/kg)	RSD (%)	difference[a] (%)
blackcurrant3	0.061	0.052	18	0.009
blackcurrant4	0.238	0.228	16	0.010
onion 1	0.169	0.129	11	0.040
onion 2	0.265	0.279	9	−0.015
potato 1	0.020	0.025	4	−0.005
potato 2	0.013	0.015	10	−0.002

[a] Difference: results obtained by automated headspace − results obtained by manual headspace.

Table 7. Results of Statistical Tests

	manual method	automated method	critical values
specificity	1.938	0.627	2.571
precision	1.007	0.083	2.000
precision	0.254	0.0004	2.571

formed for the manual method, considered as the reference method, and five extractions were carried out for the automatic method, considered as the alternative method (Table 6). Concentrations observed with these two methods are of the same order, and the differences observed are below the limit of quantification of the automated method. Moreover, the automated headspace method was more repeatable than the others, with RSD at 16 and 18% for blackcurrant and on the order of 4−11% for potato and onion matrixes. Statistical tests (Table 7) showed that headspace methods presented good precision, the calculated values were inferior to critical values: 1.007 and 0.083 for precision for manual injections (critical value is 2.0) and 0.254 and 0.0004 for precision for automated injections (critical value is 2.571).

Table 8. Recovery Rates of CS_2 in Untreated Vegetable Matrixes Spiked with DEDTC and Measured by Automated Headspace Method ($n = 5$)

	spiking level (mg/kg in CS_2)	average of recovery rates (%)	RSD (%)
blackcurrant	0.050	86	14
	0.500	101	18
onion	0.100	85	4
	0.500	85	3
potato	0.025	103	1
	0.100	103	2
	0.250	97	2

Recoveries for Automated Headspace Method. Recovery rates were calculated on potatoes, blackcurrants, and onions spiked at different levels (Table 8). The repeatability and reproducibility were very good (RSD < 20%) and the recovery rates were between 85 and 103%. The low quantity of matrix taken for analysis did not affect results observed.

CONCLUSION

The method employed to determine the amount of dithiocarbamate residues in vegetable matrixes (potatoes, blackcurrants, onions) has shown a lot of advantages. We have shown that crushing of samples allows a better homogenization and that dithiocarbamates are

not destroyed during the process. First, the manual headspace method could have been validated in compliance with norm V03-110 against the spectrophotometric method as a reference method. In the second step, we have validated the miniaturizing and the automated method in compliance with the same norm. Results obtained with this automated method were better than those obtained with the manual headspace method. The detection and quantification limits are 0.017 and 0.047 mg/kg, respectively, meeting the new dithiocarbomate MRL demands (0.050 mg/kg) for potatoes and blackcurrants. Finally, the automated and miniaturized method presents many advantages: reduction of reagent quantity used, reduction of sample preparation time, and the possibility of carrying out many analyses during a day (approximately 40).

ACKNOWLEDGMENT

The authors thank Mr. Duparque (Varian Analytical Instruments, les Ulis, France) for his technical support, and Mr. Descoins (INRA, Versailles, France) and Mr. Nicholson (Interface, Rivolet, France) for their help in the corrections of this article.

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Received for review November 2, 2000. Revised manuscript received February 21, 2001. Accepted March 2, 2001.

JF0013196