

Simultaneous Multi-Sample Supercritical-Fluid Extraction of Food Products for Lipids and Pesticide Residue Analysis†

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Received September 16, 1994; accepted in revised form December 30, 1994

Sample preparation for food analysis has traditionally involved the processing of a large number of samples simultaneously. A supercritical-fluid extraction (SFE) apparatus has been designed and tested to facilitate a similar approach, using SC-CO₂ as the extraction fluid. The prototype extractor was constructed to allow the extraction of six samples simultaneously, as well as the regulation and balancing of the fluid flow through each of the individual extraction vessels. In addition, procedures were developed to eliminate contamination from the apparatus and the extraction fluid which could interfere with electron capture detection of pesticide residues in meat samples. Rapid extraction of lipid phases from food products (soybeans, frankfurters, poultry) could be achieved within 15 minutes using extraction pressures of 5,000–10,000 psi at 60 °C and accompanying CO₂ flow rates of 5–10 L min⁻¹ (ambient conditions). Simultaneous multi-extraction of dispersed fat and soybean flake samples yielded lipid recoveries of 98 and 95%, respectively. Initial experiments on *spiked* frankfurter samples yielded analyte recoveries of 87–118% for a mixture of eight chlorinated pesticides. Additional studies on the coextraction of *incurred* organo-chlorine pesticide residues from poultry adipose tissue, resulted in 96% or better recoveries of endrin, heptachlor epoxide, and dieldrin, at the 1–3 ppm level in the extracted fat.

Keywords: multi-sample extraction, pesticides, lipids, supercritical fluid

INTRODUCTION

Supercritical-fluid extraction (SFE) is normally conducted in a laboratory environment in a mode involving single, repetitive extractions. To achieve this end, a number of devices have been constructed and reported in the literature.¹⁻³ Recently, instrumentation has become available for performing analytical-scale extractions

involving the multiple extraction of a number of samples, ranging from 2 to 44 in principle.⁴⁻⁶

However, many analytical laboratories have developed methodology in which samples are processed in a parallel fashion, that is, the Soxhlet extraction of environmental samples or the determination of fat levels in food-related matrices. In these cases, personnel are reluctant to change protocols to accommodate or integrate SFE into their respective laboratories. Therefore, an analytical SFE apparatus that will permit the simultaneous extraction of multiple samples would be welcomed.

In this study, we report on an initial prototype instrument that is capable of extracting up to six samples

† Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

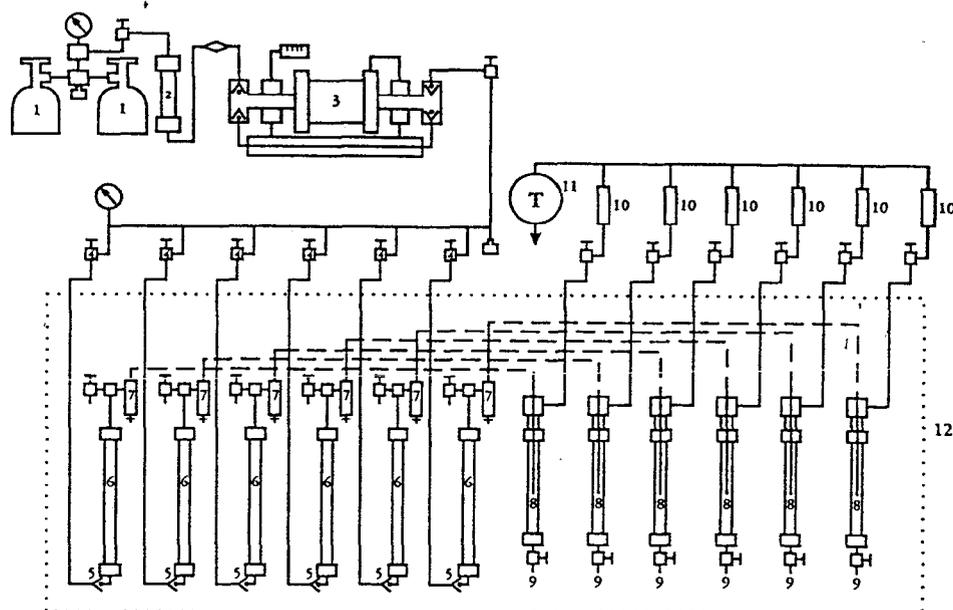


Figure 1. Schematic of multi-sample extractor: (1) compressed gas cylinders, (2) CO₂ cleanup trap, (3) gas booster compressor, (4) micrometering valve, (5) check valve, (6) extraction vessel, (7) pressure relief valve, (8) receiver vessel, (9) on/off valve, (10) rotameter, (II) dry test meter, and (12) circulating forced air oven.

simultaneously, in a parallel mode. The described extractor can be easily scaled to accommodate sample sizes ranging from 5–10 g to 100–200 g by adjusting the size of the extraction vessel. Provisions were made for using inexpensive welding grade CO₂ with the unit by incorporating a cleanup trap into the extractor design. Hence, the unit can process large samples that are more representative of complex sample matrices, such as natural products or foods. The extractor also offers the convenience of allowing the scientist to make multiple solubility determinations in one experimental run at different pressures and flow rates, since the gas flow rate and extraction pressure can be varied for each extraction channel. However, the current studies were designed to yield identical, reproducible extractions across all six extraction vessels, for either the determination of oil/fat levels in food products or pesticide residue content in such products.

EXPERIMENTAL

Extraction Apparatus. Figure 1 is a detailed schematic of the experimental apparatus used in these studies. The extraction fluid was supplied from cylinders containing gaseous carbon dioxide (National Welding Supply, Bloomington, IL). The extraction fluid was passed through a cleanup trap prior to entering the gas booster pump (Model AG 60/150, Haskel, Inc., Burbank, CA). The cleanup trap (61-cm length × 1.59-cm i.d.) consisted of a 316 stainless steel tube, rated at 70 MPa (Autoclave Engineers, Erie, PA) packed with Alumina C sorbent (Cat. No. 02103-99, Universal Scientific, Inc., Atlanta, GA), conditioned at 230 °C for four hours to maximize sorption capacity. The cleanup trap facilitated the removal of trace hydrocarbons (over a period of 2–3

months, depending on usage) in the welding grade CO₂ that interfered with the analysis of the pesticides by a gas chromatographic (GC) method employing electron capture detection (ECD).⁷

The gas booster pump was selected for its ability to produce the optimal extraction pressure commensurate with the extraction of lipids from food and natural product matrices.⁸ The chosen pump could easily deliver flow rates of 5–20 L min⁻¹ (as measured at ambient conditions) and had a delivery capacity of up to 160 L min⁻¹ across the multiple extraction channels. This high throughput of extraction fluid combined with the requisite extraction pressures produced very rapid extractions of lipid moieties from relatively large sample sizes of varying oil or fat content.

The pressurized extraction fluid next entered a distributing manifold where its entry into each individual extraction channel was controlled by a micrometering valve (Part No. 10VRMM2812, Autoclave Engineers, Inc.) mounted on top of a thermostated oven. The overall system pressure was determined by a Bourdon tube pressure gauge (Part No. P-0487-4G, Autoclave Engineers).

After passage through the micrometering valves, the extraction fluid entered a thermostated, air circulation oven having internal dimensions of 61-cm width × 61-cm depth × 90 cm in height (Model No. LAC 2-12, Despatch Industries, Inc., Minneapolis, MN). All of the system components from this point on to the exit of the extraction fluid from the receiver vessels were contained in the above oven held to ±1 °C (as indicated by the dotted line in Figure 1). To facilitate the entry and exit of the fluid delivery lines in and out of the oven, two slots (11 cm × 52 cm) were cut in the top of the oven and overlaid with

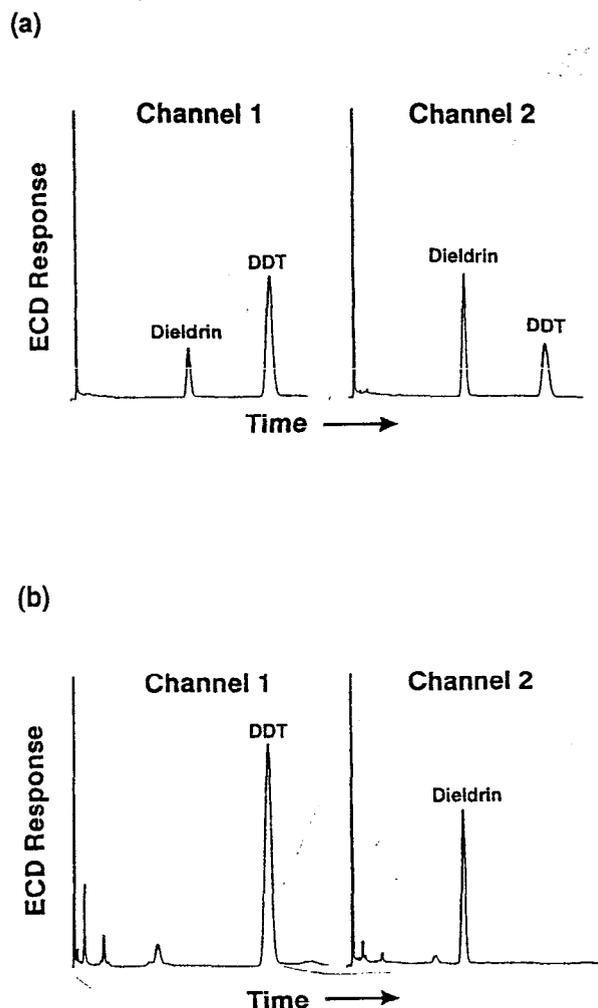


Figure 2. Electron capture detector (ECD) chromatograms of extracts from multiple sample extractor: (a) without check valves, (b) with check valves.

sheet metal. Holes for the transfer lines were then drilled in the sheet metal panels. A 1.3-m length of tubing, slightly coiled, between the oven entrance portal and the check valves, was used to equilibrate the CO_2 to oven temperature in each extraction channel.

Critical to the operation of the parallel, multi-sample extractor was the insertion of a check valve (Part No. SWO 2200 Autoclave Engineers, Inc.) to prevent back-mixing of the extraction fluid in each channel. Separate experiments run on a previously described extraction apparatus,⁹ using two extraction vessels in parallel indicated that cross-channel contamination was possible, particularly in the isolation of trace analytes. This was demonstrated by inserting a 20-g sample of lard spiked with 114 ppm of DDT into one extractor, along with a 55 ppm lard sample spiked with dieldrin, into the other extraction vessel. The extraction of the spiked lard samples was done at 62 MPa and 80 °C with a CO_2 flow of 17–18 L min^{-1} (ambient) for 60 min.

Figure 2a is the GC/ECD chromatogram when using the extractor without the check valves inserted upstream from the extraction vessels. This result clearly demonstrates that cross contamination of the resultant extracts is occurring as shown by the presence of both pesticide peaks in the extracts from either extraction channel. The cross contamination was eliminated by inserting the above type of check valve into the inlet side of each extractor vessel, yielding the results shown in Figure 2b. This extraction was run under identical conditions as those used in Figure 2a. In this case, each pesticide moiety was contained in the extraction channel in which it was originally placed.

The extraction vessels were fabricated from 316 SS, rated at 70 MPa, having dimensions of 30.5-cm length, 2.54-cm o.d., and 1.75-cm i.d (Part No. CNLX 16012-316, Autoclave Engineers, Inc.). These were held vertically on a support rack in a parallel array with the extraction fluid entering the vessel from the bottom, after undergoing equilibration in the oven. Pressure was maintained on the extraction vessels by means of a high-pressure regulating relief valve (Part No. 15700-26, Haskel, Inc.). An on/off valve was inserted at the exit tee of the extractor vessel to allow venting of the extractor. The combination of the inlet micrometering valves and the exit regulating relief valves on each separate side of the extractor vessel allowed equal and stable flows to be achieved through each extraction channel by adjusting both valves.

The extract dissolved in the supercritical fluid was transferred to the corresponding receiver vessel (dashed lines in Figure 1) by 0.318-cm high-pressure tubing, rated at 80 MPa. The tubing was inserted into the receiver vessel through a tee (approximately 26 cm into the vessel) to facilitate collection of the extract in the lower half of the receiver vessel. The extracted analytes and fat/oil pass through the regulating relief valve and down into the receiver vessel via the tubing, where they are precipitated for eventual collection. The receiver vessel was a prefabricated nipple: 20.3-cm long, 2.54-cm o.d., and 1.75-cm i.d. (Part No. CNLX 1608, Autoclave Engineers, Inc.), of 316 SS, rated to withstand 70 MPa. An on/off valve was attached to the bottom of the receiver vessel to allow collection of the extracted material. This can be done sequentially on a time as well as a fluid volume basis to collect discrete sample fractions.

The depressurized extraction fluid was conveyed to the top of the receiver vessel where it exited the oven through an on/off valve into a six-channel rotameter assembly (Model No. 1370 CA1A6 AAA, Brooks Instrument Division, Hatfield, PA) calibrated to read CO_2 flow from 3.4–34.8 standard L min^{-1} . The rotameter assembly allowed approximate monitoring of the gas flow from each of the individual extraction channels. The total flow from all or any individual extraction channel was

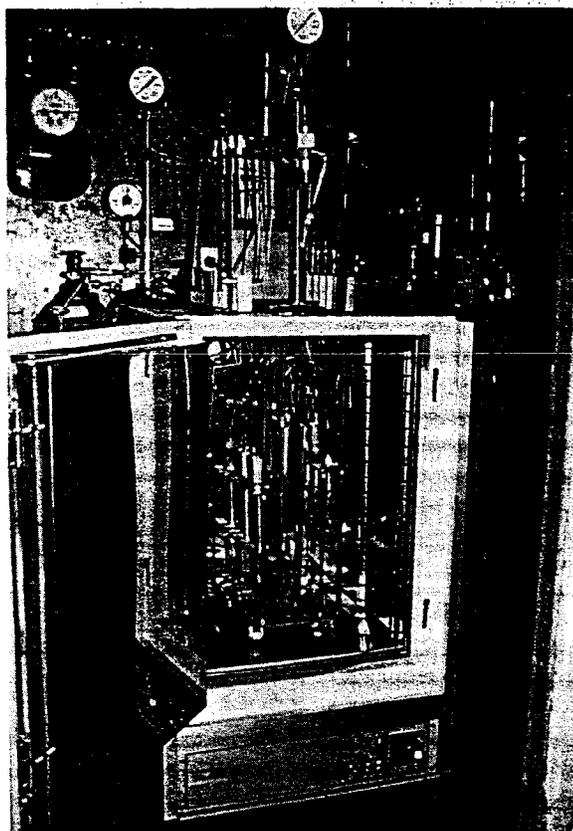


Figure 3. Photograph of the multi-sample extractor with mobile extraction vessel assembly inside oven.

measured by a dry test meter (Model DTM 200-4, American Meter Division, Philadelphia, PA), connected to the exit of the manifold where gas flow from all of the separate extraction channels was collected.

To facilitate removal of the extraction and collection vessels from the oven, the array of vessels was mounted along with the back-pressure regulators and associated on/off valves on a portable stand on casters to allow removal of the entire assembly in one piece from the oven (see Figure 3). This stand, which had templates cut and tie rods attached to hold the vessels in a vertical position, could be rolled out of the oven both before and after an extraction, merely by tightening or loosening the 0.318 cm, o.d. tubing connected to the extraction/receiving vessels from the external components attached on the outside of the oven. A cart was eventually built to allow the portable stand to be rolled right out onto the cart surface for disassembly of the extractor.

Sample Preparation and Extraction Procedure. Duplicate extractions of a lard sample were performed on all six extractor channels to monitor the performance of the multi-sample extractor. The lard sample was suspended on glass wool that was spread out on a cylindrical sheet metal insert. Five grams of molten lard were then poured over the glass wool. The sample and insert were then refrigerated before being inserted into

the extraction cells, in order to avoid any loss of sample. Extractions were carried out at 70 MPa and 60 °C at 10 L min⁻¹ (ambient) for 50 min.

To simulate trace pesticide levels in a meat product, pesticide spikes were added to 20 g of blended frankfurters by addition of 40 μL of a standard solution containing eight pesticides at concentrations between 12–60 ug mL⁻¹. This produced spike levels between 0.024 and 0.120 ppm of the following pesticides in the comminuted frankfurter matrix: α-BHC, γ-BHC, heptachlor, chlorpyrifos, heptachlor epoxide, *cis*-chlordane, dieldrin, and endrin. Eight grams of Hydromatrix (Varian, Harbor City, CA)¹⁰ were added and mixed with the frankfurter matrix using a spatula. The mixture was then transferred to the extraction cell and contained by the insertion of glass wool plugs at the top and bottom of the cell. SFE was performed on these samples at 70 MPa and 60 °C. Typically, the extraction of all six samples was run for a total of 15 min using a flow rate of 5 L min⁻¹ on each extraction channel, for a total of 450 L of CO₂ as measured at ambient conditions. Upon completion of the extraction, the gas booster pump was shut off and the pressure on the receiving vessels was allowed to drop to ambient pressure while the cells were in the heated oven. This permitted the lipid extract to be withdrawn from the receiver vessel as a liquid by simply opening the on/off valve at the bottom of vessel, and collecting the extract into a tared bottle.

Chicken adipose tissue samples containing three incurred organo-chlorine pesticide residues were also extracted in this study. Conditions of 70 MPa and 60 °C using a flow rate of 5 L min⁻¹ for 15 min proved sufficient for extraction of this sample. The peritoneal fat samples were extracted in different runs using either glass wool or Hydromatrix as sample dispersants. The quantities of chicken fat required for these different experiments required that samples from two different birds be used in the extractions. However, previous studies¹¹ have shown that these adipose tissue samples contain similar amounts of the incurred pesticide residues from all the birds used in the same feeding study.

Flaked soybeans¹² were also extracted in duplicate runs on the multi-sample extractor. The oil content and moisture level of the flakes were 19.1 and 14.7 wt %, respectively. Extraction conditions of 70 MPa and 60 °C were utilized. A run time of 15 min was used in performing the extraction, based on the known equilibrium solubility of soybean oil triglycerides in SC-CO₂,¹³ the above percentage of oil in the flake sample, and the flow rate of 5 L min⁻¹, which was utilized for the extractions. In theory, only 10.6 min would have been required for exhaustive delipidation of the soybean flakes.

Analytical Procedure. Extracts containing the pesticide residues dissolved in the fat were cleaned up using an alumina column to separate the fat from the pesticide fraction.¹⁴ Extracts from the frankfurter samples were concentrated to 1 mL by evaporation under N₂, be-

fore injection into the gas chromatograph. For the analyses of the incurred residues in poultry fat, a 2-mL sample was used with the addition of a 2 mL of a 100 pg/uL aldrin internal standard.

The pesticide content of the resultant extracts were analyzed by gas chromatography using a Hewlett Packard Model 5890 gas chromatograph (Hewlett Packard, Wilmington, DE), equipped with an electron capture detector and automatic sample injector. The pesticides were separated on a DB-5, 30 m \times 0.32-mm id. fused silica capillary column (J & W Scientific, Folsom, CA), using a temperature programmed run as follows: isothermal hold for one minute at 100 °C, temperature ramped to 250 °C at 3 °C min⁻¹, with a final isothermal hold at 250 °C for 20 min. A 2- μ L splitless injection was used for the analysis.

RESULTS AND DISCUSSION

The primary objective of the described experimental runs was to achieve reproducible analytical results across all extraction channels. This was accomplished by using the same sample in all of the extraction cells during any individual run. Achievement of this goal was ultimately linked to having equal and reproducible flow rates through each extractor channel.

During the course of the above extractions, several adjustments and improvements were made to the system to achieve the above goal. Gas leakage at the check or back-pressure relief valves was eliminated by using nitrile rubber O-rings which proved resistant to swelling in the dense carbon dioxide. Flow rates and extraction temperature/pressure were optimized so as to prevent entrainment of the extracted fat and dissolved analytes in the fluid after pressure reduction in the receiver vessel. It was found at 80 °C and flow rates in excess of 10 L min⁻¹, that lipid matter was sufficiently entrained in the decompressed gas, which lead to fat deposition in the interconnecting tubing up to and in the rotameter module. A temperature of 60 °C, along with reduction of the fluid flow rate to 5 L min⁻¹, was found to minimize this entrainment problem. Removal of collected lipid matter in the receiver vessel can in most cases be achieved by opening the on/off valve at the bottom of the receiver vessel; however, heating of the receiver vessel may also be required to remove additional lipid that does not flow out of the vessel.

Cleanup of the multi-sample extractor parts and flow path was initially required in order to minimize artifacts that interfered in the analysis of trace pesticide levels via electron capture detector. This was accomplished by washing the parts in a soap solution, followed by a thorough rinsing with water, drying, and a final rinsing with hexane. Finally, each extractor channel was flushed with SC-CO₂ at 51.7 MPa and 60 °C for 90 min at 10 L min⁻¹ to remove any additional accumulated residues.

During the extraction of the chicken adipose tissue, it was discovered that frequently only 80–90 wt % of the available fat was recovered from the samples. Independent

experiments run on the previously described screening extractor showed that chicken fat, suspended on the support glass wool, resulted in only a 84.5% recovery, while identical extraction experiments on the same fat samples supported on Hydromatrix yielded 99.6% recovery. Apparently, inadequate contact and channeling of the extraction fluid occurs when glass wool is used as a support material; therefore, Hydromatrix is preferred for most extractions.

The results for the extraction of pure lard using the multi-sample extractors were most gratifying. The first run of six samples simultaneously yielded an average recovery of 101% (based on the initial gravimetric charge) and a relative standard deviation of 2.7%. Similarly, a second set of extractions run on the unit under approximately identical conditions produced an average recovery of 98.2% over the six extraction channels and a relative standard deviation of 2.5%. The range of lard recoveries were from 96.46–104.14% on the first set of extractions and 94.91–100.0% on the second run. This consistency indicates that approximately the same flow rate is being achieved on each individual extraction channel.

Extraction of oil from soyflakes was also done in duplicate runs on the multi-sample extractor. The first run yielded an average value of 96.8% oil recovery with a relative standard deviation of 2.39% between the six extraction channels. The second set of extractions produced an average recovery of 95.4% over all six extraction channels and a 2.90% relative standard deviation. The total volume of CO₂ used in the initial run as measured by the gas totalizer was 445 L, which when divided by the total extraction time yielded a flow rate of 29.74 L min⁻¹. This compares favorable with the actual flow readings taken during the extraction, which averaged 30.04 L min⁻¹, testimony to the reproducibility of the flow conditions during the extraction. Similar results were also recorded during the second trial run where the average flow rate per minute from the gas totalizer summation was 29.6 L min⁻¹ vs. an average of 30.3 L min⁻¹ for individual readings.

Multi-sample extraction of spiked frankfurter matrix was conducted three times using all six extraction channels. Table I summarizes the recoveries achieved for the pesticides at the listed spiking level for the three experimental runs. The data suggest that the spiked pesticide moieties can be successfully coextracted from the frankfurter matrix along with the fat. Some of the listed recoveries are relatively high (120%) and the variation in the recovery data relative to 100% recovery quite wide. Part of the dispersion is due to the GC/ECD analytical method, since the data presented in Table I are the average of three individual GC/ECD analyses. Statistical analysis of the precision for individual pesticide recoveries across all six extraction channels per run had relative standard deviations ranging between 6–13% as listed in Table I. Another source of error contributing to the dispersion in the recovery results in Table I is the spiking procedure.

TABLE I
Recovery and Precision of Multi-Sample Extraction of Pesticides in Fortified Frankfurters

Pesticide	Spike (ppm)	Run #1		Run #2		Run #3	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
α -BHC	0.024	98.5	6.2	98.5	11.7	99.1	8.0
γ -BHC	0.040	94.1	6.7	85.2	11.7	96.1	9.6
Heptachlor	0.040	112.4	8.0	110.4	13.0	116.7	11.1
Chlorpyrifos	0.120	115.7	9.1	125.6	11.1	105.1	7.5
HC-epoxide	0.080	101.9	8.2	96.7	13.0	101.1	8.7
Chlordane	0.080	104.5	7.0	120.5	11.8	107.8	7.6
Dieldrin	0.120	112.6	8.8	100.7	12.9	104.5	7.8
Endrin	0.120	116.6	6.8	122.6	13.6	108.6	7.8

TABLE II
Analytical Results for Incurred Residues in Chicken Sample (T325) from Multiple Sample Extractor Experiment

Sample	Heptachlor Epoxide		Dieldrin		Endrin	
Before Extraction	0.63*	(100%)**	2.18	(100%)	2.09	(100%)
1	0.51	(81.0%)	1.83	(83.9%)	1.84	(88.0%)
2	0.54	(85.7%)	1.85	(84.9%)	1.83	(87.6%)
3	0.52	(82.5%)	1.85	(84.9%)	1.81	(86.6%)
4	0.52	(82.5%)	2.24	(103%)	1.79	(85.6%)
5	0.62	(88.9%)	2.25	(103%)	1.84	(88.0%)
6	0.62	(98.4%)	2.53	(116%)	2.04	(97.6%)
<u>Average</u> Glass Wool Support	0.545	(86.5%)	2.07	(96.0%)	1.86	(88.9%)

* ppm

** % recovery

Despite careful spiking of the frankfurter matrix using a μ L-syringe to measure the aliquots of pesticide standard, there is undoubtedly some error from this source in the recovery data.

The average fat recovery from the frankfurter matrix (27.12% fat) over the three reported runs (Table I) plus a blank run, was over 91% under these extraction conditions. The pesticide recovery data in Table I shows that most of the pesticides were adequately recovered under the same extraction conditions. It has been previously shown that total extraction of the fat in a meat matrix is not a prerequisite for attaining high recoveries of the pesticide content in such a matrix.¹⁵

Initial studies on the extraction of poultry adipose tissue were conducted on tissue from a chicken coded T325. An extraction performed on the multi-sample unit using glass wool to disperse the chicken fat yielded the results shown in Table II. The recoveries were all above

80%, averaging between 86–96% recovery for the three pesticides, noted by numbers in the parenthesis in Table II. These recoveries were compared to the pesticide levels in the sample before extraction as determined by GC/ECD analysis, after thermal rendering and sample cleanup, as described in references 11 and 15. Similarly, another multi-sample extraction was performed on the adipose tissue from the same bird (T325), using Hydromatrix to disperse the fat prior to extraction. As shown in Table III, the recoveries tended to be somewhat higher than those achieved using the glass wool support, ranging from 89–95% recovery. In both cases (Tables II and III), separate analysis of the pesticide content of the chicken sample, before SFE, yielded similar results. This trend probably reflects the enhanced contact between the fatty tissue and SC-CO₂, afforded by mixing the sample with the Hydromatrix. Comparison of the average pesticide con-

TABLE III
Analytical Results for Incurred Residues in Chicken Sample
(T325) from Multiple Sample Extractor Experiment

Sample	Heptachlor Epoxide		Dieldrin		Endrin	
	Concentration	Recovery	Concentration	Recovery	Concentration	Recovery
Before Extraction	0.61*	(100)**	2.01	(100%)	2.03	(100%)
1	0.55	(91.7%)	1.92	(95.0%)	1.92	(95.5%)
2	0.52	(86.7%)	1.88	(93.1%)	1.87	(93.0%)
3	0.56	(93.3%)	1.96	(97.0%)	2.04	(101%)
4	0.54	(87.1%)	1.79	(89.9%)	1.83	(89.3%)
5	0.53	(85.5%)	1.81	(91.0%)	1.83	(89.3%)
6	0.56	(90.3%)	2.06	(104%)	2.06	(100%)
Average Hydromatrix Support	0.54	(89.1%)	1.90	(95.0%)	1.93	(94.7%)

* ppm

** % recovery

TABLE IV
Analytical Results for Incurred Residues in Chicken Sample
(T388) from Multiple Sample Extractor Experiment

Sample	Heptachlor Epoxide		Dieldrin		Endrin	
	Concentration	Recovery	Concentration	Recovery	Concentration	Recovery
Before Extraction	0.91*	(100)**	2.38	(100%)	2.34	(100%)
1	0.85	(93.4%)	2.26	(95.0%)	2.16	(92.3%)
2	0.85	(93.4%)	2.24	(94.1%)	2.23	(95.3%)
3	0.88	(96.7%)	2.31	(97.1%)	2.30	(98.3%)
4	0.92	(101%)	2.42	(102%)	2.40	(103%)
5	0.87	(95.6%)	2.30	(96.6%)	2.28	(97.4%)
6	0.86	(94.5%)	2.26	(95.0%)	2.26	(96.6%)
Average Hydromatrix Support	0.87	(95.8%)	2.30	(96.6%)	2.27	(97.1%)

* ppm

** % recovery

tent, determined for all six extraction channels in Tables II and III, shows good agreement for the three pesticides for these two runs.

A more extensive extraction study was next performed using the multi-sample extractor and a different poultry specimen (bird coded T388). In this case, three separate runs were initiated using the same sample containing the three incurred pesticide residues mixed with Hydromatrix. The results are reported in Tables IV, V, and VI, which include the recoveries for each pesticide from each extraction channel, the average value for each pesticide over all six channels and the pesticide content in

the adipose tissue before each extraction run. Comparison of pesticide content of the unextracted samples for the three separate runs shows excellent agreement, testimony to the homogeneity of the samples and/or reproducibility of the analytical assay method. This result allows an intracomparison to be made between the average results displayed in Tables IV, V, and VI.

Comparison of the result on each individual multi-sample run for each channel and pesticide, respectively, attests to the repeatability of the extractions. This is a direct reflection of the stability and partitioning of the SC-CO₂ over the six extraction channels. Evidence to sup-

TABLE V
Analytical Results for Incurred Residues in Chicken Sample
(T388) from Multiple Sample Extractor Experiment

Sample	Run #2					
	Heptachlor Epoxide		Dieldrin		Endrin	
Before Extraction	0.90*	(100%)**	2.37	(100%)	2.30	(100%)
1	0.99	(110%)	2.61	(110%)	2.70	(117%)
2	0.90	(100%)	2.17	(91.6%)	2.14	(93.0%)
3	1.01	(112%)	2.53	(107%)	2.51	(109%)
4	0.85	(94.4%)	2.11	(89.0%)	2.17	(94.3%)
5	0.97	(108%)	2.47	(104%)	2.43	(106%)
6	0.98	(109%)	2.45	(103%)	2.43	(106%)
Average Hydromatrix Support	0.95	(106%)	2.39	(101%)	2.40	(104%)

* ppm

** % recovery

TABLE VI
Analytical Results for Incurred Residues in Chicken Sample
(T388) from Multiple Sample Extractor Experiment

Sample	Run #3					
	Heptachlor Epoxide		Dieldrin		Endrin	
Before Extraction	0.91*	(100%)**	2.41	(100%)	2.33	(100%)
1	0.94	(103%)	2.49	(103%)	2.39	(103%)
2	0.88	(96.7%)	2.34	(97.1%)	2.25	(96.6%)
3	0.99	(109%)	2.61	(108%)	2.52	(108%)
4	0.94	(103%)	2.49	(103%)	2.41	(103%)
5	0.97	(107%)	2.55	(106%)	2.45	(105%)
6	0.95	(104%)	2.54	(105%)	2.45	(105%)
Average Hydromatrix Support	0.95	(104%)	2.50	(104%)	2.41	(104%)

* ppm

** % recovery

port this claim can be substantiated by comparing the total CO₂ output over the period of the extraction, in liters/minute, vs. the average of intermittent integral CO₂ flow rate readings during the course of the extraction. When this was done for Runs 1, 2, and 3, respectively, the overall average flow as recorded by the dry test meter was 31.1, 30.7, and 31.0 L min⁻¹. These values compare quite favorable to the average of the intermittent flow readings during the same experiments, which were 30.8, 30.9, and 32.0 L min⁻¹, respectively, for Runs 1, 2, and

3. This is strong evidence of the flow stability of the system for the quoted extraction period.

The average recovery values for each individual pesticide per run are quite satisfactory, ranging from 96–106% recovery as shown in Tables IV, V, and VI. The average absolute values for pesticide content in ppm also compare quite favorable when comparing Runs 1, 2, and 3. Based on this data, it would appear that the multi-sample extractor can be used repeatedly with confidence to reproduce accurate and precise analytical data. This con-

TABLE VII
Multi-Sample Extractor Recoveries of Incurred Residues in Chicken Sample (T388)

Residue	% Recovery	% RSD
Heptachlor Epoxide	101.7	6.3
Dieldrin	100.4	6.1
Endrin	101.6	6.5

clusion is borne out by taking the average recovery for the three pesticide moieties for the 18 extractions performed in the above runs. These recoveries are tabulated in Table VII and are 101.7, 100.4, and 101.6%, respectively, for heptachlor epoxide, dieldrin, and endrin. These recovery figures are certainly respectable and indicate the SFE has been completed. The statistical precision associated with cumulative average of all the extractions done on individual channels is approximately 6% as shown in Table VII.

CONCLUSIONS

The multi-sample extractor, described in this study, permits rapid extractions to be performed on up to six samples, simultaneously, in real time. This performance is facilitated by employing a gas booster compressor that is capable of delivering high flow rates of fluids, such as CO₂, to six extraction vessels simultaneously. Experimental data has shown that these high fluid flow rates can be partitioned equally by using the specified combination of micrometering and pressure relief valves noted in the text. Accurate and precise simultaneous extractions, performed on the same sample, have been achieved with this device for the extraction of lipids and trace pesticide moieties in two different meat matrices.

The prototype extractor, utilized in these studies, can be readily modified to accommodate different size extraction vessels and collection devices, as has already been demonstrated on a earlier extractor design, originally developed in this laboratory.¹⁶ Integration of an in situ

sample cleanup scheme or fractionation column can be conveniently added to the described unit to retard the migration of lipid matter in the supercritical fluid or alternatively aid in the fractionation of complex mixtures. Extension to multiple solubility measurements in real time can also be facilitated by adding the appropriate pressure gauges and flow monitoring devices into the extraction channel circuits, thereby allowing a range of extraction pressures to be used simultaneously under isothermal conditions.

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