Review

Matrix Solid Phase Dispersion as an Effective Preparation Method for Food Samples and Plants before HPLC Analysis

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Abstract

Karasová G., Brandšteterová E., Lachová M. (2003): **Matrix solid phase dispersion as an effective preparation method for food samples and plants before HPLC analysis**. Czech J. Food Sci., **21**: 219–234.

This review deals with a preparation technique – Matrix Solid Phase Dispersion (MSPD) and its possibilities in the HPLC analysis for contaminants, pesticides, drug residues, and natural compounds in food samples. The main principle of MSPD is explained, the important factors influencing the effectivity and recovery of this technique are discussed. The advantages and disadvantages of MSPD and other classical extraction, isolation, and purification procedures are compared. The present article provides a bibliography of MSPD applications in food sample matrices during last years for various analytes and different sample matrices.

Keywords: matrix solid phase dispersion; high performance liquid chromatography; food samples; contaminants; pesticides; drug residues; natural compounds

Matrix Solid Phase Dispersion

Matrix Solid Phase Dispersion (MSPD) was developed in 1989 (Barker *et al*. 1989) and, during recent years, this method has found again its important place among the preparation techniques applied in the analysis of plant and food samples (without or with the fat contents and with different amounts of water). This assay is also suitable for solid, semi-solid, and viscous matrices that often cause problems in other common preparation procedures. The classical preparation and clean-up methods often include more steps such as mincing and/or mechanical homogenisation, the additions of bases, acids, or abrasives, centrifugation, the transfer of the supernatant, pH adjustment, extraction, and in many cases complicated purification procedures. The last steps are dependent on the analytical method that is applied for the analyte determination. When HPLC is used, the compatibility of the solvents residues with the mobile phases is necessary.

MSPD is based on the solid phase dispersion of the sample matrix for the subsequent isolation of various analytes. By blending a matrix with a solid support, a semi-dry material is obtained. It is used as a pre-column packing from which analytes possessing various chemical properties can be isolated by the elution profile of solvents (or their mixtures) with different elution powers and polarities. The main advantage is the fact that this technique allows to perform several steps in the sample preparation simultaneously. It can be used for a multiresidual isolation from a single

matrix. MSPD is a simple approach to the disruption of biological materials. It combines the use of mechanical forces generated from the grinding of samples with irregularly shaped particles (silica or polymer based solid supports) to produce a sample/column material from which the dispersed matrix components can be selectively isolated (Barker *et al*. 1993). This isolation is different for animal cells and plant cells. Plant cell walls often require more physically and chemically dynamic procedures to achieve complete cellular disruption. Barker and co-workers developed a generic MSPD assay which can be modified according to the analytes and sample matrices. The scheme of the MSPD process is illustrated in Figure 1. The sample is placed in a glass mortar containing a solid support material and is blended with a glass pestle. The bonded phase-support acts as an abrasive, lipophilic bound solvent that assists in the sample disruption and lysis of the cell membranes. The blended material is packed as an SPE cartridge and the analytes are eluted sequentially with solvents. The sample material is distributed onto a solid support and produces a unique column material that allows a new degree of sample fractionation (Barker *et al*. 1989, 1993; Barker & Floyd 1996). MSPD is a technique very similar to SPE but the separation principle is completely different. The bound phase in the solid support provides an added dimension to the MSPD process. It acts as a solvent or detergent that dissolves and disperses the sample components. This greatly enlarges the surface area for the extraction and the sample components are distributed over the surface according to their relative polarities. It has been observed that certain analytes tend to be eluted in fractions that are not readily predictable by their relative distribution in the solid phase or eluting solvents. This can be explained by the possibility of co-elution with some matrix components in the given fraction. The retention properties of MSPD present a mixture of partition, adsorption, and ion-paired chromatography which is unique. There are many factors that affect the MSPD procedure (Barker 1998a): the solid support and the bound phase used, the nature of the sample matrix, the sample to solid support ratio, the solvent elution sequence performed, the use of matrix modifiers, the blending of the sample with acids, bases, chelatores, preservatives, or other modifiers.

The interactions between the individual components and the analysed compounds in MSPD involve the analyte with the solid support, the analyte with the bonded phase, the analyte with the dispersed matrix, the matrix with the solid support, the matrix with the bonded phase; all above components interact with the elution solvents, and these dynamic interactions act simultaneously. It is

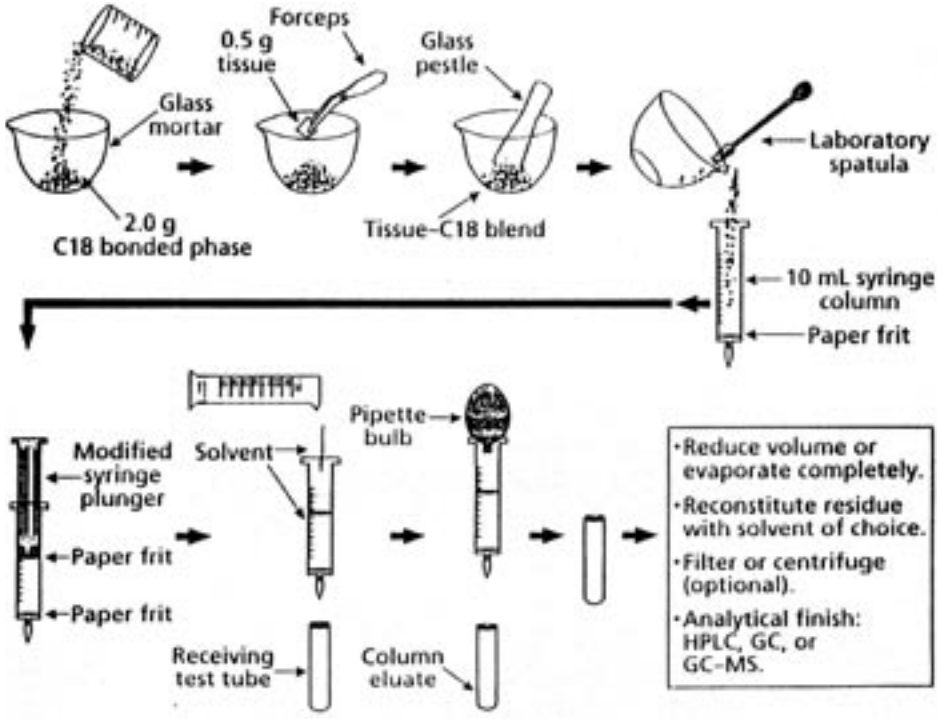

Figure 1. Flow diagram of the matrix solid-phase dispersion process (Barker 1998a)

obvious that the solid support affects the retention-elution of the analytes and the dispersed sample components. Although a volume of 8 ml is often reported to be sufficient for generic MSPD procedure, it was found that this is not always true for all eluting solvents tested and all analytes studied. It was also observed, however, that the sufficient elution is finished in 4 ml of the elution mixture which is equal to one column volume. As in SPE, the solid support, the possible bonded phase, and the elution profile are important but the effect of the sample matrix dispersed from the top to the bottom of the column is more important in MSPD. It creates a new phase. This new phase and its new interactions, in combination with the analyte distribution and its interactions, are the most controlling factors in MSPD (Barker 2000b).

Some studies confirmed the suggestion that the pore size of the sorbents is of little importance in MSPD but could vary with the sample matrix and should be considered. The particle size is a more important factor. Particles less than 20 μm can prolong the procedure time and they decrease the flow rate through the MSPD column. The particle size of 40–60 μm is optimal but sorbents with the size of about 100 μm can also be used. These materials are often less expensive. The carbon loading is recommended in the range of 8–18%. The generic sample/sorbent ratio is approximately 1:4 but it can be modified according to the chemical properties of the analytes and the consistency of the sample matrix. Similarly to SPE assay, the conditioning is very important. Precleaning of the sorbent can diminish the interferences. Sometimes the addition of acids, bases, of chelating agents can influence the washing and elution steps in the whole MSPD method. Especially in such cases where the analytes have an acidic or a basic character and/or are very polar.

The choice of the washing and eluting solvents is very important. If an additional cleaning step is necessary, it is possible to use the MSPD column with another sorbent (Florisil, Silica, Alumina) at its bottom (co-column) or to elute analytes directly from the MSPD column into a second SPE column. A simple injection without additional purification is used e.g. in the case of some pesticides or other less polar pollutants. Such isolations make MSPD suitable for the multiresidual analysis (Barker 1998b).

MSPD has already found its place as an effective preparation technique in the food analysis. S. A. Barker summarised the application of MSPD in food analysis up to the year 2000 in a review (Barker 2000a). All important facts for the practical monitoring of the biologically important compounds in real samples are given in it.

The aim of our review was to provide the information about this renovating preparation technique, dealing especially with HPLC analysis for contaminants, pesticides, drugs, and in recent years also for natural biologically active compounds present in plants and food samples. MSPD has a generic character for many analytes in different sample matrices. It provides results equivalent to other classical pre-separation methods. However, MSPD generally requires by 95% less solvent, and by about 90% less time than these classical methods. It is the main reason why this method has also found its important place in the food analysis, especially in the connection with the very effective and universal HPLC technique. The applications of MSPD in this field are summarised in the following text, and MSPD and HPLC conditions are listed in Tables 1–3.

The technique of MSPD has mostly been applied in the monitoring of food contaminants, i.e. compounds whose presence is in admissible or whose concentrations are limited to very low levels. The main matrices are food samples (fruits, vegetables, tissue and milk products having solid, semi-solid, or viscous consistencies). Only few papers are interested in the applications of MSPD before the analysis of natural compounds. More papers have described the determination of pesticides and drugs as the main contaminants in food samples. The compounds such as pesticides are mostly not very polar, thus not all the steps suggested by the authors of MSPD assay have to be used. Solvents with medium polarity (methylene chloride, chloroform) or their mixtures with more polar solvents (acetone, acetonitrile, ethyl acetate) are sufficient for the elution of these compounds from the food matrices. So, the whole MSPD procedure is not so complicated, mainly in combination with GC or HPLC often using the direct MSPD extract injection. Only in some cases is it necessary to evaporate the elution mixture which does not present any problem when these kinds of organic solvents are used. More complications can occur if more polar analytes are quantified. More polar solvents, often with the pH adjustment, have to be applied which complicates the direct injection into the HPLC columns. Moreover, in GC these solvents are completely prohibited.

Table 1. The conditions of MSPD and HPLC analysis of contaminants in fruits and vegetables

Compound	Matrix	MSPD		HPLC			References
		sorbent	elution agent	stationary phase	mobile phase	detection	
Abamectin	orange	C18	methylene chloride	C18	MeOH/water	ESI-MS	Valenzuela *et al*. (2000)
Abamectin	citrus fruit	C18	methylene chloride	C18	MeOH/water, ACN/ water, MeOH/water	UV, FL, ESI-MS	Valenzuela *et al*. (2001a)
Diflubenzuron, hexaflumuron, flufenoxuron, hexathiazox, benfuracarb	orange	C8	methylene chloride	C18	ACN/water MeOH/water	UV, APCI-MS	Valenzuela *et al*. (2001b)
Carbamate, benfuracarb, diflubenzuron, flufenoxuron, hexaflumuron	citrus fruit	C8, C18	methylene chloride	C18	ACN/water	UV	Valenzuela *et al*. (1999)
Carbamates	orange, grape, onion, tomato	C8	methylene chloride/ACN (3:2, v/v)	C8	MeOH/water, ACN/ water, water/acetic acid, water/NaCl	APCI-MS, ESI-MS	Fernández *et al*. (2000)
Cichloran, flutriafol, *o*-phenyl-phenol, prochloraz, tolcofos methyl	orange, lemon, banana, pepper, chard, onion	C8	methylene chloride	C18	MeOH/water	APCI-MS	Blasco *et al*. (2002a)
Bitertanol, carbendazim, fenthion, flusilazole, hexythiazox, imidacloprid, methidathion, metho-carb, pyriproxyfen, trichlorfon	orange	C8, C18	methylene chloride	C18	MeOH/water	APCI-MS	Blasco *et al*. (2002b)
Imidacloprid, metalaxyl, myclo-butanil, thiabendazole, propham	strawberry, orange, potato, pear, melon	C8	methylene chloride	C18	MeOH/ammonium formate	APCI-MS	Pous *et al*. (2001)
Flupoxam, linuron, rimsulfuron, diflubenzuron, fenoxycarb, metho-myl, tetradifon, benomyl, carben-dazim, thiophanate methyl	broad bean, carrot, celery, green pea, leek, potato, champignon, apple, lettuce, strawberry, rye, black currant, cherry, cucumber, cereals	silica gel	*n*-hexane/diethyl ether, methanol/ methylene chloride	in clean up columns: phenyl; C8; C18; in analytical columns: C18; C8	ACN/water MeOH/ water	UV-DAD	Michel & Buzewski (2002)
Carbendazim	careals	silica gel	methanol/ methylene chloride (1:5, v/v)	in clean up column: C8; in analytical column: C18	MeOH/water	UV-DAD	Michel & Buzewski (2003)
Aflatoxins: B1, B2, G1, G2	peanuts	C18	ACN	C18	water/ACN	FL, API-MS	Blesa *et al*. (2003)

Another problem is caused by the fact that all fractions of the MSPD assay can contain groups of analytes with different chemical properties and, of course, at different concentration levels, too. It means that the development for more groups of analytes in one-matrix samples is much more complicated and only the realisation of blank experiments can increase the demands for the time of the preparation process.

RESIDUES OF CONTAMINANTS IN FOOD SAMPLES

Pesticides in fruit and vegetables

Non-modified as well as modified supports were applied in the MSPD assay for different fruits and vegetables in recent years (Sherma 1997). According to the author, the pesticide isolation from these matrices is not very complicated. The differences in the results obtained with various sorbents were not very great and, consequently, only some small corrections of the original MSPD procedure had to be realised also for different kinds of fruits and vegetables using methylene chloride as the eluting solvent. HPLC has been recommended as the best method of the choice for the subsequent analysis (MSPD and HPLC conditions are mentioned in Table 1).

Abamectin residues in citrus fruits were analysed by HPLC after the MSPD preparation step (Valenzuela *et al*. 2000, 2001a). Also in this case methylene chloride was sufficient for the quantitative elution of contaminants with a high recovery of bout 94%. The combinations of UV, fluorescence, and MS (with electrospray interface) detectors were compared after the HPLC analysis. The quantification limit was 0.5 μg/kg. The same authors (Valenzuela *et al*. 2001b) tested also different supports for the MSPD assay for the determination of the residues of benzoylphenylurea and carbamate insecticides in fruits. More than 150 orange fruit samples were analysed and LC/UV and LC/APCI/MS were applied for their determination. C8 was evaluated as the more efficient sorbent and methylene chloride as the eluting solvent. The extraction recoveries varied from 74% to 84% and the detection limits were better with LC/APCI/MS than with LC/UV.

Previously, the same authors obtained very interesting results in the optimisation assays for different parameters, such as the type of solid support for MSPD during the determination of some urea and carbamate insecticides also in citrus fruits (Valenzuela *et al*. 1999). They tested cellulose, silica, C2, C8, C18, CN bonded phase, graphitised carbon black (GCB), and they slightly modified the MSPD conditions. The authors recommended C8 and C18 as the main sorbents while some other sorbents were placed at the bottom of the glass column for MSPD (cellulose, silica, GCB, CN).

The efficiencies of different solid phases (C8, C18, CN, NH_2, and phenyl) in MSPD were also tested and compared in LC/MS analysis of 13 carbamates in oranges, grapes, onions, tomatoes (Fernández *et al*. 2000). The mixture of methylene chloride and acetonitrile (3:2, v/v) was used for the elution. The use of silica at the bottom of the glass column for MSPD was also tested. The main recoveries using C8 varied from 64% to 106%.

HPLC of five fungicide residues in oranges, lemons, bananas, peppers, chards and onions was described (Blasco *et al*. 2002a). The residues were extracted by MSPD using C8 sorbent and the recoveries were 52.5%–91.1%. The same authors developed an LC/MS for the determination of bitertanol, carbendazim, fenthion, flusilazole and other pesticides in oranges (Blasco *et al*. 2002b). Two preparation procedures were tested and compared; one of them was MSPD, which provided high recoveries of 47%–96% in a wide range of the concentrations of the analytes. The results were also compared with those of the liquid extraction (ethyl acetate).

Many pesticides are compounds with heterogeneous structures. One insecticide (imidacloprid), three fungicides (metalaxyl, myclobutanil, thiabendazole) and one herbicide (propham) were analysed simultaneously in strawberries, oranges, potatoes, pears, and melons by MSPD followed by LC/APCI/MS. C8 sorbent and methylene chloride were used for MSPD (Pous *et al*. 2001).

HPLC determination of the pesticide residues from matrices was used after LLE, SPE and MSPD preseparation techniques which were tested and compared (Michel & Buszewski 2002). Ten herbicide, insecticide and fungicide residues in fruits, vegetables and cereals were evaluated. HPLC with DAD and on-line switching preparation-separation mode was used. In comparison to GC-based techniques, RP-HPLC with UV detection proved to be more suitable for the determination of polar, non-volatile, and termolabile pesticides. MSPD reached the highest extraction recoveries. Silica was used as an effective sorbent. The time

Table 2. The conditions of MSPD and HPLC analysis of drug residues and environmental pollutants in milk and tissues

Compound	Matrix	MSPD		HPLC			References
		sorbent	elution agent	stationary phase	mobile phase	detection	
7 benzimidazole anthelmintics	milk	C18	methylene chloride/ethyl acetate (1:2, v/v)	C18	phosphoric acid/ACN	UV-DAD	Long *et al.* (1989)
8 sulfonamides	milk	C18	methylene chloride	C18	orthophosphoric acid/ACN	UV-DAD	Long *et al.* (1990a)
Tetracyclines	milk	C18	ethyl acetate/ACN (1:3, v/v)	C18	oxalic acid/ACN	UV-DAD	Long *et al.* (1990b)
Clorsulon	milk	C18	ethyl ether	C18	NaH_2PO_4 buffer/ACN	UV	Schenck *et al.* (1991)
Benzimidazole anthelmintics	milk	C18	methylene chloride/ethyl acetate (1:2, v/v), methylene chloride	C18	phosphoric acid/ACN; NaH_2PO_4 buffer/ACN oxalic acid/ACN	UV-DAD	Barker & Long (1994)
Furazolidone, chloramphenicol, chlorsulon tetracyclines, sulfonamides antimicrobials	milk and infant formula		ethyl acetate, ethyl ether, ethyl acetate/ACN (1:3, v/v), methylene chloride				
Sulfadimethoxine	catfish muscle tissue	C18	methylene chloride	C18	phosphoric acid/ACN	UV-DAD	Long *et al.* (1990d)
5 benzimidazole anthelmintics	beef liver tissue	C18	ACN	C18	phosphoric acid/ACN	UV-DAD	Long *et al.* (1990e)
5 sulfonamides	salomon muscle tissue	C18	methylene chloride	C18	ACN/ammonium acetate	UV-DAD	Reimer & Suarez (1992)
Sulphonamides	bovine and porcine muscle	C18	methylene chloride	C18	sodium acetate (buffered with acetic acid)/ACN	UV-DAD	Walker *et al.* (1992)
Ivermectin	bovine liver tissue	C18	methylene chloride/ethyl acetate (3:1, v/v)	C18	MeOH/water	FL	Schenck *et al.* (1992a)
Nicarbazin	chicken tissue	C18, C8, cyclohexyl	ACN	C18	not identified	UV	Schenck *et al.* (1992b)
Tetracyclines	meat, milk, cheese	C18	ethyl acetate/ACN (1:3, v/v)	C18	MeOH/ACN/oxalic acid	UV-DAD	Brandšteterová *et al.* (1997)
10 antibiotics, 2 anthelmintics, 1 coccidiostat, 1 chemotherapeutic drug	pork and veal meat	C18	1 methylene chloride 2 ethyl acetate	C18	ammonium acetate buffer + ACN/MeOH	UV-DAD FL	Le Boulaire *et al.* (1997)

Table 2 to be continued

Compound	Matrix	MSPD		HPLC			References
		sorbent	elution agent	stationary phase	mobile phase	detection	
10 antibiotics, 2 anthelmintics, 1 coccidiostat, 1 chemotherapeutic drug	pork and veal meat	C18	1 methylene chloride 2 ethyl acetate	C18	ammonium acetate buffer + ACN/MeOH	UV-DAD FL	Le Boulaire *et al.* (1997)
Clenbuterol	bovine liver	C18	ACN with 1% (v/v) acetic acid	RP	water/MeOH with TFA	ECD IT-MS	Crescenzi *et al.* (2001)
6 sulfonamides	chicken muscle tissue	neutral aluminium oxide	70% (v/v) aqueous e thanol solution	silica based RP	acetic acid solution in water/ACN/DMF	UV-DAD	Kishida & Furusawa (2001)
Linear alcohol ethoxylates	fish tissue	C18	1 hexane, 2 ethyl acetate and ethyl acetate/MeOH (1:1, v/v), 3 MeOH	C18	ACN/water	FL	Tolls *et al.* (1999a)
Alkylbenzenesulfonate (LAS), sulfophenyl-carboxylic acids (SPC)	fish tissue	C18	1 hexane, 2 ethyl acetate, 3 ethyl acetate/MeOH (1:1, v/v), 4 MeOH, 5 MeOH/ water (1:1, v/v)	C18	ACN/water/$NaClO_4$ ACN/TBA-HSO_4	FL	Tolls *et al.* (1999b)
Alkylphenol ethoxylates, alkylphenols	fish and muscle samples	C18	MeOH	C18	MeOH/water	FL	Zhao *et al.* (1999)
DBP	rainbow-trout diet	C18	hexane/benzene (4:1, v/v)	C8	ACN/water	FL	Loveland *et al.* (2001)

required for the sample preparation was very short and the consumption of solvents was very low in comparison with LLE and SPE. Column switching technique enables to simplify the whole assay and this technique is more and more frequently applied in the routine HPLC analysis.

Michel and Buszewski (2003) coupled MSPD with HPLC and column switching for the determination and quantification of the systemic fungicide – carbendazim residue in cereals. Silica was used for MSPD and was modified by the addition of HCl. The analyte was eluted from the extraction column with methanol-methylene chloride mixture (1:5, v/v). The recoveries ranged from 84% to 90.7%. The application and the mechanism of sorption on the modified silica gel for the sampling of carbendazim from cereals were also discussed.

Aflatoxins are toxic metabolites produced during food spoilage by the fungi *Aspergillus*. MSPD extraction was used to determine aflatoxins B1, B2, G1 and G2 from peanuts (Blesa *et al*. 2003). Optimisation was carried out of different parameters such as the type of solid support for the matrix dispersion and the eluting solvents. The extraction method used 2 g of peanut sample, 2 g of solid-phase, and acetonitrile (20 ml) as the eluting solvent. Various solid phases were tested for MSPD (silica, phenyl, C8 and C18). The best recoveries for all aflatoxins (between 78% and 86% with RSD 4–7%) were obtained using C18 bonded silica. The limits of quantification ranged from 0.125 to 2.5 ng/g using LC with fluorescence detection. In addition, LC coupled to mass spectrometry with an electrospray interface was used for the confirmation of the presence of aflatoxins in real samples.

Drug residues in milk and animal tissues

In 1989–1994, the MSPD method was widely used for the isolation of drug residues from milk and animal tissues prior to HPLC analysis.

Benzimidazole anthelmintics (Long *et al*. 1989), sulfonamides (Long *et al*. 1990a), tetracyclines (Long *et al*. 1990b) and clorsulon (Schenck *et al*. 1991) were extracted from milk. The extraction was performed by a slightly modified MSPD method using C18 sorbent proposed by Barker *et al*. (1989). The eluates were analysed using HPLC with UV detection.

Benzimidazole anthelminitics were eluted from C18/milk matrix column with methylene chloride-ethyl acetate (1:2, v/v). The recoveries ranged from 70% to 107%. Eight sulfonamides were eluted with methylene chloride achieving recoveries of 73.1%–93.7%. Oxytetracycline, tetracycline, and chlortetracycline were eluted with ethyl acetate-acetonitrile (1:3, v/v) with recoveries of 63.5%–93.3%. The elution of chlorsulon from C18/milk matrix cartridge was achieved with ethyl ether. The eluate was cleaned with Florisil SPE and the overall recovery was 93%. Barker and Long (1994) used the generic extraction procedure for several drugs (benzimidazole anthelmintics, chloramphenicol, chlorsulon, furazolidone, sulfonamide antimicrobials in milk and infant formula, tetracyclines) used in dairy production. In all cases the sorbent Bulk C18 was used and the analytes were eluted from the extraction cartridge with an appropriate solvent.

This generic method was also applied for the sample preparation in HPLC/UV analysis of drugs in animal tissues. Long and co-workers used it for the isolation of oxytetracycline (Long *et al.* 1990c) and sulfadimethoxine (Long *et al.* 1990d) from catfish muscle tissue. Oxytetracycline was eluted from MSPD column with acetonitrile-methanol (1:1, v/v) and sulfadimethoxine with methylene chloride. The recovery was 80.9% and 101.1%, respectively. Also five benzimidazole anthelmintics were extracted from fortified beef liver with the eluting solvent acetonitrile; the recoveries ranged between 62.0%–86.8% (Long *et al.* 1990e).

Sulfonamides were isolated from salmon muscle tissue (Reimer & Suarez 1992) and bovine and porcine muscle (Walker *et al*. 1992). The elution solvent was methylene chloride and the extraction recoveries were 66%–82% with the salmon tissue and 37%–85% with bovine and porcine muscle, respectively.

Ivermectine residues were extracted from bovine liver tissue (Schenck *et al*. 1992a). Elution was performed with methylene chloride-ethyl acetate (3:1, v/v) and, after purification with alumina SPE, the analysis was carried out using HPLC with fluorescence detection. The recovery was 74.6%.

Purification using alumina cartridge was also used in MSPD of nicarbazin from chicken liver and muscle tissue prior to HPLC/UV analysis (Schenck *et al*. 1992b). Nicarbazin was eluted from the C18/tissue matrix column with acetonitrile yielding recoveries of 95.8% and 83.7% for liver and muscle, respectively. In an effort to test the ruggedness of the MSPD extraction procedure, C18 obtained from three manufacturers plus two other sorbents, C8 and cyclohexyl, were employed in the method. The

results showed that the recoveries of nicarbazin from liver tissue were the same regardless of the sorbent used.

In the last seven years, only few works were focused on the HPLC determination of drug residues in food samples using MSPD as the sample preparation method. In 1997, Solid Phase Extraction (SPE) and MSPD were tested as pre-separation techniques for HPLC determination of tetracycline antibiotics (TCs) in our laboratory (Brandšteterová *et al*. 1997). The aim of the study was to compare these two methods as the pre-concentration possibilities prior to HPLC monitoring of TCs in meat, milk and cheese. MSPD-HPLC was recommended as an alternative to SPE-HPLC for the determination of TCs in milk. Milk samples were blended with C18 sorbent in the presence of oxalic acid and ethylenediamine disodium tetraacetic acid. TCs were eluted with 10 ml ethyl acetate-acetonitrile (1:3, v/v). The extraction recoveries were 63.5–93.3%, i.e. higher than when using SPE but the detection limit for TCs using MSPD was a little lower than for other pre-separation techniques. The comparison of SPE and MSPD confirmed the advantages of MSPD for TC determination in milk.

Le Boulaire *et al*. (1997) made a comparison between the MSPD technique with solvent or buffer extraction and liquid/liquid transfer, usually practised in the residue analysis. 14 veterinary drug residues (10 antibiotics, 2 anthelmintics, 1 coccidiostat, and 1 other chemotherapeutic drug) were determined by HPLC in pork and veal. Analytes were extracted using C18 sorbent. Two fractions were collected by elution with 1-methylene chloride and 2-ethyl acetate. UV and fluorescent detections were used. The recoveries were 40–60%. Many advantages of MSPD in comparison to LLE were mentioned: higher extraction yields, a lower solvent consumption, time saving, a lower need of laboratory equipment, and also the possibility of the automation of the method.

A few years later, Crescenzi *et al*. (2001) investigated the possibility of combining MSPD with molecularly imprinted solid-phase extraction (MISPE). They determined clenbuterol in bovine liver. C18 sorbent was used for MSPD. The mixture of C18 and the liver sample was packed into an SPE cartridge and placed on the top of MISPE cartridge. Clenbuterol was eluted from the MSPD cartridge into the MISPE cartridge using acetonitrile containing 1% acetic acid. The ability of the molecularly imprinted polymer to selectively adsorb the analyte in acetonitrile was exploited for re-extracting clenbuterol directly from this acetonitrile extract via the double cartridge tandem system. The analyte was eluted from the MISPE cartridge with acidified methanol. A clear eluate was evaporated, redissolved, and analysed by HPLC using electrochemical detection (ECD) or ion trap mass spectrometry (LC/IT-MS). The complete extraction was rapid, and recoveries exceeded 90%.

The neutral aluminium oxide was used for MSPD isolation of 6 sulphonamides (SAs) from chicken prior to HPLC analysis (Kishida & Furusawa 2001). Other polar sorbents were also tested (basic and acid aluminium oxide, silica gel, and Florisil). Ethanol was used as the eluting solvent because of low toxicity. The sorbents were deactivated by the addition of water to the eluent. SAs were isolated in only one step, i.e. elution with a 70% (v/v) aqueous ethanol solution. The recoveries were higher than 80% while low recoveries were obtained using a non-polar sorbent C18. In addition, the C18-MSPD technique required sorbent conditioning and C18-tissue matrix washing for the isolation of SAs from animal tissues. MSPD and HPLC conditions are listed in Table 2.

Environmental pollutants in animal tissues

MSPD was also applied as a sample preparation method in the analysis of some environmental pollutants (surfactants from laundry detergents, polycyclic aromatic hydrocarbons PAHs). Tolls *et al*. (1999a) described the isolation of surfactants – alcohol ethoxylates from fish using MSPD. The extraction with C18 sorbent and aluminium oxide purification allowed the recoveries to reach 75% plus. The eluting solvents were 1-hexane, 2-ethyl acetate and ethyl acetate-methanol (1:1, v/v), and 3-methanol. Three fractions were obtained. After purification and derivatisation, the extracts were analysed by HPLC using fluorescent detection.

Tolls *et al*. (1999b) determined another surfactant – linear alkylbenzensulfonate (LAS) and its sulfophenylcarboxylic acid metabolites (SPC) in fish samples. The combination of MSPD with C18 sorbent and ion-pair liquid-liquid partitioning (IP-LL) of the extracts was used for LAS. The recovery of LAS from the spiked sample exceeded 70% using fractional elution. The column was eluted sequentially with hexane, ethyl acetate, ethyl acetate-methanol (1:1, v/v), methanol, and methanol-water (1:1, v/v) yielding 5 fractions. In

a simultaneous determination of LAS and SPC, MSPD was used with subsequent isolation of SPC with graphitised carbon black SPE and IP-LL of LAS. The recoveries were 84% for LAS and 65% for SPC. HPLC with fluorescent detector was used for the quantification.

MSPD with sequential purification was developed to isolate and purify non-ionic surfactants alkylphenol ethoxylates (APEs) and alkylphenols in both fish and muscle samples (Zhao *et al*. 1999). The elution profile, sequential purification, and experimental set up were optimised. C18 was used as the solid-phase for the matrix dispersion. Methanol was found to be the optimal eluting solvent for APEs. Aluminium oxide was quite efficient for the removal of the coeluting interferences. The recoveries were higher than 92%. Quantitative analysis was done using RP-HPLC with fluorescent detection.

Dibenzo[*a,l*]pyrene (DBP), one of the polycyclic aromatic hydrocarbons was determined in experimental rainbow-trout diets (Loveland *et al*. 2001). The sample was blended with C18 sorbent and benzo[*a*]pyrene internal standard was added to the mixture. Extraction and purification were accomplished in a single step by extracting the sample mixture with hexane-benzene (4:1, v/v) from a cartridge containing 2 g Florisil. The determination was performed with HPLC on C8 bonded phase column with fluorescent detection. The mean analytical recovery of DBP from spiked samples was 101–107% (RSD 1–7%).

Natural compounds in food and plant samples

Not many papers dealing with the application of MSPD as a pre-separation technique for the analysis for natural compounds present in food and plant samples were published. Especially in such cases where more polar analytes are monitored and so more individual steps or different combinations of washing and eluting solvents are required. Moreover, a lot of less polar interferences can occur in sample matrices and often many other purification steps are necessary to be included. But, in recent years, the use of MSPD occurred in the procedures developed for the naturally present analytes in these kinds of samples.

The determination of β-carotene in medical food was described with the use of HPLC with MSPD (Chase *et al*. 1999a). The nutrient was extracted from the medical food without saponification by MSPD and quantified by isocratic normal-phase chromatography using silica column and n-hexane modified by isopropyl alcohol as the mobile phase. There are no current official methods for such kind of analysis, of carotene in medical food; AOAC Method 941.14 is available for carotenes in fresh plant material. But in this method carotene is extracted with acetone and hexane using an open-column chromatography technique. Some European procedures are also applicable to complex foods and to total carotenoids in fruit, vegetables and beverages (Eitenmiller & Landen 1998). The sorbent Bondesil C18 was used for MSPD assay (2 g) with 0.5 g of sample applied in the procedure. The MSPD cartridge was washed with 7 ml of *n*-hexane containing 0.5% (v/v) isopropyl alcohol, followed by 7 ml of methylene chloride-ethyl acetate-*n*-hexane mixture (3:3:4, v/v/v) containing 0.5% (v/v) isopropyl alcohol. After the evaporation of the combined extracts to dryness, the residue was dissolved in 1 ml of *n*-hexane and injected onto the HPLC column. Extraction recovery was about 91.2%, CV 0.50–3.10%.

LC and MSPD were recommended for the analysis of all-rac-α-tocopheryl-acetate and retinyl palmitate in milk-based infant formula (Chase & Long 1998). The vitamins were extracted without saponification by means of MSPD and determined also by means of normal HPLC with fluorescence detection. Retinyl palmitate and vitamin E were analysed using isocratic elution with *n*-hexane with the addition of isopropyl alcohol. Recoveries were 96.8% for retinyl palmitate and 91.5% for all-rac-α-tocopheryl acetate, respectively. The Bondesil C18 was used for the MSPD assay. The authors added 100 µl of isopropyl palmitate gently blended with a pestle. This addition to C18 as a modifier was necessary for the efficient elution of retinyl palmitate from MSPD cartridge. The first elution step was realised with 7 ml of 0.5% (v/v) isopropanol in *n*-hexane and 7 ml of methylene chloride. After evaporation and dissolution of the residue in *n*-hexane, the residue was analysed by HPLC with the fluorescence detection.

In 1999 Chase with co-workers (Chase *et al*. 1999b) described a liquid chromatography method for the analysis of retinyl acetate in soy-based infant formula using MSPD. Retinyl acetate is sometimes used as the vitamin A source in formulated products. The AOAC International method did not provide methodology for the analysis of vitamin A in soy-based infant formulas. Methods available

able 3. The conditions of MSPD and HPLC analysis of natural compounds in food and plant samples

Compound	Matrix	MSPD		HPLC			References
		sorbent	elution agent	stationary phase	mobile phase	detection	
β-carotene	medical food	C18	hexane with 0.5% (v/v) isopropanol; methylene chloride/ethyl acetate/hexane (3:3:4, v/v/v) with 0.5% (v/v) isopropanol	Si 60	hexane/isopropanol	UV	Chase *et al.* (1999a)
All-rac-α-tocopheryl acetate, retinyl palmitate	milk-based infant formula	C18	hexane with 0.5% (v/v) isopropanol; methylene chloride	Si 60	hexane with 0.5% (v/v) isopropanol or with 0.125% (v/v) isopropanol	FL	Chase & Long (1998)
Retinyl acetate	soy-based infant formula	C18	hexane with 0.5% (v/v) isopropanol; methylene chloride	Si 60	hexane with 0.28% (v/v) isopropanol	FL	Chase *et al.* (1999b)
Vitamin K1	milk-based infant formula	C18	hexane with 0.5% (v/v) isopropanol; ethyl acetate	C8	reductive ionic solution* in MeoH/hexane	FL	Chase *et al.* (1999b)
Vitamin K1	soy-based infant formula	C18	hexane with 0.5% (v/v) isopropanol; ethyl acetate	C8	reductive ionic solution * in MeoH/hexane	FL	Chase *et al.* (2000a)
Vitamin K1	medical food	C18	hexane with 0.5% (v/v) isopropanol, ethyl acetate, methylene chloride	C18	reductive ionic solution * in MeoH/hexane	FL	Chase *et al.* (2000b)
Vitamin K1	medical food	C18	ethyl acetate (ASE extr. parameters)	C18	reductive ionic solution * in MeoH/hexane	FL	Chase & Thompson (2000)
Asterosaponin	starfish-*Asterias rubens*	C18	water/ACN (1:1, v/v)	C18	ammonium formate in D_2O/ACN	UV, ESI-MS, NMR	Sandvoss *et al.* (2001)
Lutein, zeaxanthin	spinach leaves	C30	acetone	C30	acetone/water	UV, APCI-MS, NMR	Glaser *et al.* (2003)
Rosmarinic, caffeic and protocatechuic acid	plant *Melissa officinalis*	C18	MeOH/water pH 2.5 (4:1, v/v)	C18	MeOH/water pH 2.5	DAD-UV	Žiaková *et al.* (2003)

*reductive ionic solution – 2.0M zinc chloride, 1.0M sodium acetate and 1.0M acetic acid per litre of methanol

for the analysis of vitamin A in milk-based infant formula are often applied, however, matrix differences exist and thus the validation of this method for soy-based infant formula was required. The MSPD procedure was the same as in the analysis of retinyl palmitate (Chase & Long 1998). Extraction recoveries were 94.7%.

The same authors (Chase *et al*. 1999c) published also HPLC determination of vitamin K1 in milk-based infant formula. Vitamin K1 is converted to a fluorescent hydroquinone with a post-column zinc reductive reactor. Vitamin K1 is unstable under alkaline conditions and cannot, consequently, withstand the saponification (Eitenmiller & Landen 1999). The use of postcolumn chemical reduction of the quinone to the fluorescent hydroquinone allows selective and sensitive quantification of vitamin K1 after SPE on silica and/or C18 and reversed-phase HPLC. The current AOAC Method 992.27 based on the pre-treatment with ammonium hydroxide and methanol followed by the extraction with methylene chloride-isooctane (2:1) and open column chromatography on silica is required for the purification of the extracts. MSPD procedure is a very slightly modified generic MSPD assay discussed till now. The first elution solvent was again 0.5% (v/v) isopropanol in *n*-hexane (9 ml), the second one ethyl acetate (9 ml). Both eluates were combined, evaporated, and the residue was reconstituted in 1 ml of *n*-hexane. The extraction recoveries for vitamin K1 were in the range of 86.4–101%, CV 0.5–6.7%.

The same method was used for the determination of vitamin K1 in soy-based infant formula (Chase *et al*. 2000a). The current AOAC International Method 992.27 for the determination of vitamin K1 suffers from high CVs and cannot be used for infant formula samples containing corn oil. The MSPD procedure and HPLC analysis as applied for milk-based infant formula were validated for soy-based infant formula. The recoveries obtained were 92.5%.

Vitamin K1 was analysed also in medical food samples again using MSPD for the extraction (Chase *et al*. 2000b). Recoveries were on averaged 97.9%, the limit of detection was 6.6 pg and that of quantification 22 pg on column. Due to the sample matrix differences related to the milk-based infant formula (lipid interference), the method has to be modified. Thus the issues of solvent polarity, miscibility, or partitioning characteristics become critically important in the MSPD method development. The medical food matrix is highly complex and may contain different protein and fat combinations and amounts. This study differed from the earlier work by incorporating the addition of two drops of a reductive ion solution to the sample once it was weighed onto the C18/isopropyl palmitate mix. This addition precipitated the proteins, allowing the eluting solvents to flow freely through the cartridge.

Accelerated Solvent Extraction (ASE) was used in a combination with MSPD assay for the determination of vitamin K1 in medical food (Chase & Thompson 2000). The medical food sample was treated equally as in the MSPD procedure, followed by ASE for the hands-free automated extraction. Vitamin K1 in the ASE extract was then determined by HPLC using fluorescence detection. ASE is a relatively newly developed technology that can reduce the extraction time and the solvent consumption as well as to increase the yield. Samples are loaded onto the ASE system and the solvent is pumped into an extraction cell which is then pressurised and heated for several minutes. The coupling of these two techniques automates the MSPD assay and makes the whole preparation procedure much more selective and sensitive. The extraction recoveries were nearly 100% in all analytical experiments. This method provides a completely new area of the isolation possibilities, as the necessity of using 3 different solvents is eliminated with ASE in which one solvent only is applied.

Combinations of MSPD and direct on-line LC-NMR, LC-MS and LC-NMR-MS were tested for the rapid screening of natural products, i.e. asterosaponin fraction, in starfish *Asterias rubens* (Sandvoss *et al*. 2001). In this report, this new analytical approach was applied for the first time. MSPD represents a significant simplification compared to classical extraction procedures. It yields suitable extracts for LC-NMR-MS in one simple preparation step, while LC-NMR-MS yields a wealth of information in one chromatographic run. Asterosaponins are a group of new biologically active steroids isolated from natural sources and they contain a large number of similar compounds which are difficult to separate. MSPD can thus simplify the preseparation process. The pieces of fish were mixed with water and C18 sorbent. Washing was carried out with water and the natural compounds were eluted with increasing amounts of acetonitrile. The elution was assisted by a slight excess pressure of nitro-

gen. The fraction containing asterosaponins was eluted with water-acetonitrile (1:1, v/v). From 5 g starfish material, 11 mg of asterosaponin fraction was obtained. MSPD is much more simple than the authors' initial procedure which consisted of a two-fold 16 h acetonitrile extraction, ultrasonic treatment, centrifugation and preparative chromatographic purification (Sandvoss *et al*. 2000). Furthermore, MSPD allows a miniaturisation of the extraction step, complementing the analytical scale LC-NMR-MS hyphenation.

Qualitative and quantitative determination of carotenoid stereoisomers in a variety of spinach samples using MSPD before HPLC-UV, HPLC-APCI-MS and HPLC-NMR on-line coupling was described by Glaser *et al*. (2003). Carotenoids lutenin and zeaxanthin were isolated by MSPD and then determined using C30 HPLC column. These carotenoids can be found in many dark-green vegetables as spinach, broccoli, and kale; they are not produced in the human body. Recent studies revealed that the bio availability of β-carotene from spinach is low and highly dependent on the food matrix. Spinach leaves were washed by deionised water, frozen in liquid nitrogen and ground with a pestle. Spinach (0.5 g) was then mixed with 1.5 g of MSPD C30 sorbent (30–50 μm). MSPD cartridge was conditioned with 15 ml of water and polar impurities were eluted with another 5 ml of water-methanol mixture. After drying the column, carotenoids were eluted with acetone until the extract became colourless (less than 500 μl). Recoveries were about 98%. Chromatograms were artefact free.

The first paper concerning the application of MSPD as an effective preparation technique for the monitoring of phenolic acids in medical plants was published in 2003 (Žiaková *et al*. 2003). Three phenolic acids (rosmarinic, caffeic, and protocatechuic) were isolated by MSPD with about 90% extraction from *Melissa officinalis* and determined by HPLC-DAD. Different MSPD sorbents and various elution agents were tested and optimal extraction conditions were evaluated. Many other preparation techniques were studied by the authors as preparation procedures (LLE, SPE, ASE, SFE) (Čaniová & Brandšteterová 2001, 2002) and the results were compared. Seven different sorbents and their combinations were chosen for the MSPD development. Dried plant tops were ground to powder and an aliquot was mixed with 2 g of previously cleaned sorbent and 1 ml *n*-hexane. The mixture was homogenised and transferred into a 10 ml syringe. The interfering compounds were washed out with 10 ml of n-hexane, followed by 10 ml of methylene chloride, and after drying the syringe for 5 min under vacuum phenolic acids were eluted with eluting mixtures tested (methanol, methanol and 0.2% v/v HCOOH, methanol-water, pH 2.5, 80:20 v/v, methanol-water 60:40 v/v, and ethylacetate). After the evaporation to dryness, the residues were dissolved in methanol-water, pH 2.5, (80:20 v/v), and injected onto the HPLC column. Gradient elution was applied for the quantitation. The extraction recoveries of all compounds analysed were evaluated for various volumes of different eluting solvents. Although, the volume of 10 ml is often reported to be sufficient for generic MSPD procedure, it was found that this is not always true for all eluting solvents tested and all analytes studied. In some cases more than 20 ml of elution mixtures was necessary to obtain a higher recovery. In these cases the eluates have to be preconcentrated, especiallly for the analytes present in low concentrations in the medical plants analysed.

MSPD has been demostrated to be a suitable preparation technique, a simple alternative to LLE, SPE and SFE, for the isolation of phenolics from natural plant materials. No homogenisation, grinding or milling steps are necessary. It is only recommended to select suitable eluting agents giving the highest yields of the analytes, and to optimise the volume of the eluting medium. The washing step can be modified according to the amounts of the interfering and co-eluting compounds. The MSPD procedure can be modified very simply for the isolation of another phenolics in other plant materials. HPLC conditions are showed in Table 3.

Abbreviations

ACN	acetonitrile
APCI	atmospheric pressure chemical ionisation
APE	alkylphenol ethoxylate
ASE	accelerated solvent extraction
CV	coefficient of variation
DAD	diode array detector
DBP	dibenzo[*a*,*l*]pyrene
ECD	electrochemical detection
ESI	electrospray interface
FL	fluorescent detection
GC	gas chromatography
GCB	graphitised carbon black

grad. gradient elution
HPLC high performance liquid chromatography
IP-LL ion-pair liquid-liquid partition
IT/MS ion trap mass spectrometry
LAS linear alkylbenzensulfonate
LC liquid chromatography
LLE liquid-liquid extraction
MeOH methanol
MISPE molecularly imprinted solid-phase extraction
MS mass spectrometry
MSPD matrix solid-phase dispersion
NMR nuclear magnetic resonance
PAH polyaromatic hydrocarbon
RP reversed phase
RSD relative standard deviation
SFE supercritical fluid extraction
SPC sulfophenylcarboxylic acid metabolite
SPE solid phase extraction
TC tetracycline
UV ultraviolet

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Received for publication August 20, 2003
Accepted after corrections November 5, 2003

Súhrn

Karasová G., Brandšteterová E., Lachová M. (2003): **Matrix solid phase disperzia – efektívna metóda pre úpravu potravinových a rastlinných vzoriek pre HPLC analýzu**. Czech J. Food Sci., **21**: 219–2340.

Prehľadný článok sa zaoberá technikou úpravy vzorky – Matrix solid phase disperziou (MSPD) a možnosťami jej využitia v HPLC analýze kontaminantov, pesticídov, rezíduí liečiv a prírodných látok v potravinových vzorkách. V práci je vysvetlený princíp MSPD, zhodnotené sú tu hlavné faktory ovplyvňujúce efektívnosť a výťažnosť tejto metódy, ako aj výhody a nevýhody MSPD v porovnaní s inými klasickými metódami extrakcie, izolácie a prečistenia analytov. Uvádza sa tu tiež prehľad aplikácií MSPD pri analýze rôznych analytov v rôznych potravinových vzorkách, publikovaných v posledných rokoch.

Kľúčové slová: matrix solid phase disperzia; vysokoúčinná kvapalinová chromatografia; potravinové vzorky; kontaminanty; pesticídy; rezíduá liečiv; prírodné látky

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