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Review

Applications of matrix solid-phase dispersion in food analysis

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Abstract

Matrix solid-phase dispersion (MSPD), a patented process for the simultaneous disruption and extraction of solid and semi-solid samples, was first reported in 1989. Since that time, MSPD has found application in numerous fields, but has proven to be particularly applicable for the analysis of drugs, pollutants, pesticides and other components in foods. The present article provides a review of these and related applications and discusses both the practical and theoretical aspects for the use of MSPD in sample processing. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Food analysis; Matrix solid-phase dispersion; Extraction methods; Pesticides; Drugs

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1. Introduction

The past decade has seen many innovations in the analytical processes that can be applied to prepare foods for extraction and determination of drugs, pollutants and naturally occurring substances. This has resulted in the recognition that older methods can now be replaced with protocols that are faster, less expensive and that perform equal-to or better-than classical methods.

For example, a new process for the simultaneous disruption and extraction of semi-solid and solid samples was introduced in 1989 [1] and has been almost exclusively applied to the analysis of drugs and pollutants in foods. This process, matrix solid-phase dispersion (MSPD), combines several related analytical techniques, performing sample disruption while simultaneously generating a chromatographic material that possesses a unique character (see Refs. [2–9] for reviews) for target analyte isolation.

The application of MSPD for the analysis of foods is based on the blending of a viscous, solid or semi-solid sample with an abrasive solid support material that has been derivatized to produce a bound organic phase (for example, octadecylsilyl or C_{18}) on its surface, such as silica-based solid-phase extraction (SPE) materials. This process is similar to the classical use of sand as an abrasive, wherein the shearing forces of blending a sample and a solid

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material using a manual or mechanical device disrupt the gross architecture of the sample, breaking the sample components into smaller pieces. However, in MSPD the bound organic phase provides an added dimension to the process. The bound organic phase acts like a solvent or detergent that dissolves and disperses sample components into the bound phase, thus accomplishing complete disruption of the sample and its dispersion over the support surface. This greatly enhances surface area for extraction of the sample. Sample components would be expected to distribute over the surface and into this phase based on their relative polarities. The non-polar components would disperse into the non-polar organic phase and would be effected by the dynamic changes that occur as this process proceeds. Smaller, more polar molecules (water) would be expected to associate with silanols on and in the silica particle as well as with matrix components capable of hydrogen bonding. The larger, less polar molecules are envisioned as distributing across the surface of this multi-phasic structure.

The disruption and dispersion accomplished by MSPD has been observed by scanning-electron microscopy (SEM) [1]. The photomicrographs of bonded-phase solid support particles (silica based, C_{18}) typically used in the process show that these materials have sharp edges, as opposed to the spherical packings used in LC columns, that would assist in shearing during mechanical blending. Examination of SEM photomicrographs of underivatized silica particles following blending with liver tissue, for example, show an obvious disruption of sample architecture, resulting only in the generation of clumps of cells. The component cells do not themselves appear to be disrupted. Cellular disruption and complete dispersion of a sample, including component cells, is evident when C_{18} derivatized materials are used, however [1,2,5].

2. Performing a MSPD extraction

The application of MSPD to sample disruption and extraction has proven to be quite generic. It has been applied to human blood samples, animal tissues (oysters, crayfish, fish, bovine, porcine, ovine, etc.), milk, infant formula, bacteria, apples, oranges, pears, tomatoes, lettuces, paprikas, corn and fortified medical foods. The process requires simple devices and can be readily performed in the laboratory or in the field. Thus, a viscous, semi-solid or solid sample can be placed in a glass mortar containing a bonded-phase solid support material and mechanically blended with a glass pestle to attain complete disruption and dispersal of the sample. This MSPD blend is sufficiently dry (in part due to the absorption of water by the silica) to pack a column for performing chromatographic elution to isolate target analytes or other sample components. This general approach has proven to be applicable to a wide range of food matrices and types of analytes (Table 1) [10–81].

As seen from Table 1, MSPD has been most frequently applied to the isolation of veterinary drugs from the milk and tissues of food animals. More recently, MSPD has found application to the analysis of herbicides, pesticides and other pollutants from fruits and vegetables as well as processed foods. These applications of the method have, in general, employed a small sample (approximately 0.5 g) blended with a glass mortar and pestle using 2.0 g of a bonded-phase solid support (a 4:1 ratio of support-to-sample), typically C_8 or C_{18}. Milk has been blended by simply placing the sample in a test tube and mixing the sample and solid support with a spatula or related device. Solid samples processed through a blender or some other homogenizing step may similarly be prepared.

Once blending is complete, the blend is transferred to a column (often constructed from a syringe barrel or some other appropriate device) containing a frit that retains the entire sample. A second frit (paper disc) is often placed on top of the material before compression, which is accomplished by using a modified syringe plunger. Although MSPD has unique chromatographic properties, the classic principles of performing good chromatography still apply: one should avoid channels in the column and not over-compress or compact the material.

Addition of eluting solvent to the column may be preceded by use of the solvent (typically 8 ml) to backwash the mortar and pestle. Evidence indicates that most target analytes are eluted in the first 4 ml of a MSPD column formed from 0.5 g of sample and 2 g of solid support. Most MSPD elutions have been reported to be conducted by gravity flow, with flow

Table 1
Applications of MSPD to the analysis of foods

Analyte(s)	Matrix	Ref.	Analyte(s)	Matrix	Ref.
Alkylphenol ethoxylates	Tissues	[10]	Pesticides	Beef fat	[44]
Aminoglycosides	Bovine kidney	[11]		Catfish muscle	[45]
Antibacterials	Foods, review	[12]		Crayfish	[46]
Benzimidazoles	Animal tissues	[13]		Fish	[47]
	Bovine liver	[14]		Fruit, vegetables	[48]
	Swine muscle	[15]		Milk	[49]
	Bovine milk	[16]		Oranges	[50]
	Calf tissues	[17]		Oysters	[51]
	Bovine milk	[18]		Vegetables	[52]
β-Agonists	Bovine liver	[19]		Fish	[53]
	Bovine liver	[20]		Plant materials	[54]
β-Carotene	Medical foods	[21]		Fruits and vegetables	[55]
Carbofuran	Corn	[22]		Citrus fruits	[56]
Chloramphenicol	Milk	[23]		Human serum	[57]
Chlorsulfuron	Milk	[24]		Citrus fruits	[58]
Chlorsulon	Milk	[25]	Pollutants	Aquatic species	[59]
	Milk	[26]	Pyrethroids	Vegetables	[60]
Clenbuterol	Bovine liver	[27]	Sulfa drugs	Chicken tissues	[61]
	Liver	[28]	Sulfadimethoxine	Catfish	[62]
Drug residues	Animal tissues	[1]		Catfish	[63]
	Animal tissues	[2]		Catfish muscle	[64]
	Animal tissues	[7]		Catfish, plasma	[65]
	Animal tissues	[6]	Sulfamethazine	Animal tissues	[66]
	Foods	[3]		Swine tissues	[67]
	Milk	[29]		Swine tissues	[68]
Drugs, pollutants	Aquatic species	[30]	Sulfonamides	Animal tissues	[69]
Furazolidone	Chicken muscle	[31]		Infant formula	[70]
	Milk	[32]		Meat, milk	[71]
	Swine muscle	[33]		Milk	[72]
Ivermectin	Fish muscle	[34]		Salmon muscle	[73]
	Milk	[35]		Salmon muscle	[74]
	Liver	[36]		Swine muscle	[75]
Moxidectin	Bovine tissues	[37]		Tissues, milk, eggs	[76]
Nicarbazin	Animal tissues	[38]		Bovine, swine tissues	[77]
Oxamyl, methomyl	Fruits	[39]	Tetracyclines	Foods	[78]
Oxolinic acid	Catfish	[40]		Milk	[79]
Oxytetracycline	Catfish muscle	[41]	Vitamins	Medical foods	[80]
PCBs	Fish	[42]		Infant formula	[81]
PCBs, pesticides	Fish	[43]			

being initiated by the application of pressure to the head of the column using a rubber bulb or by the brief use of a vacuum box.

Many MSPD procedures have also employed the use of co-columns to obtain further fractionation and to assist in sample clean-up. A co-column material (Florisil or silica, for example) can be packed in the bottom of the same column as the MSPD material or used as an external column. Such columns may be literally stacked so as to collect and further fractionate the sample as it elutes from the MSPD column.

MSPD has also proven to be applicable to the isolation of several drugs within a class or several classes of drugs from a single sample. Since the entire sample is blended into the column it is possible to perform multiple or, particularly, sequential elution of the sample. This permits isolation of a single compound, a class of compounds or even

several classes of compounds from the sample. Data have been presented that illustrate the complete fractionation of the entire contents of a sample and has been applied to the isolation and identification of endogenous components [82–84] of bacteria.

MSPD is, at its roots, a form of chromatography and the general principles of the science apply. However, MSPD is quite different from, for example, SPE. MSPD, as opposed to all other forms of chromatography, is designed to disrupt and disperse the components of solid samples into a bound organic phase on a solid support, subsequently being used as a column packing material from which sample components may be eluted. Unlike SPE or other forms of chromatography, the sample is dispersed throughout the column, becoming part of the overall chromatographic character of the system. MSPD, in essence, takes advantage of this process of dispersing the entire sample throughout the entire column, creating a unique chromatographic phase.

The dynamic interactions that occur between all of these components are not completely understood and further research in this regard is needed. However, several factors have been shown to effect performance and are, for the most part, the same factors that are known to influence the performance of most chromatographic procedures. These are (1) the nature of the solid support (silica versus polymeric, pore size, endcapping), (2) the nature of the bonded phase (normal-phase versus reversed-phase, total carbon content), (3) pretreatment or modification of the sample (pH adjustments, etc.), (4) the nature and sequence of elution solvent addition and (5), most specifically for MSPD, the nature of the sample matrix.

There is little doubt that the presence and chemical character of the bonded phase plays a significant role in MSPD. A lipophilic bonded-phase is thought to be essential to performing both sample disruption and dispersion. This lipophilic phase is fundamental to the formation of a new phase that is, essentially, a membrane bi-layer assembly, giving the MSPD material its unique chromatographic characteristics.

Since the sample matrix becomes part of the chromatographic phase in MSPD, it would not be surprising to discover that the results and recovery for a given analyte from one matrix to another would significantly vary, say bovine liver to apples. This may prove to be the case for some analytes and matrices but little data exist upon which to state this as fact. Nonetheless, the theoretical aspects and interactions of lipid content, total protein, etc., and their distribution may be reflected in MSPD performance.

While the bonded-phase on the solid support is immobile, the dispersed matrix components are subject to elution. Indeed, in MSPD applications the fractionation of the entire sample, as demonstrated by mass-balance experiments, may be accomplished. Matrix components themselves are eluted in certain fractions. It has been observed that certain target analytes tend to be eluted in fractions that are not readily predictable by their relative distributions in a solid-phase or eluting solvent. This is explained, perhaps, by the possibility that certain analytes will be consistently co-eluted with certain matrix components in a given fraction. However, the co-elutants are potential interferences in the final analysis and can often be removed by the use of co-columns or simple extraction as previously described.

3. Conclusion

MSPD is a distinct analytical process for sample disruption and dispersion that, nonetheless, possesses many of the characteristics of other chromatographic methods. However, its ability to simultaneously disrupt and disperse semi-solid and solid samples over a bonded-phase solid support that may subsequently be used as a column packing that possesses a unique chromatographic character that provides a new dimension of sample fractionation, makes MSPD unique. The application of MSPD to difficult analytical problems in food analysis can greatly reduce analyst time, increase sample throughput and shorten turn-around time. The reduction in solvent use and the expense of purchase and disposal, as well as providing analytical results that are equal to or better than classical or ''official'' methods, make MSPD an attractive alternative approach to such analyses. Concerns about small sample size and the corresponding decrease in sensitivity and homogeneity have been addressed. Sensitivity has been enhanced, not by increasing sample size but by the development of new analytical instrument tech-

nologies. Homogeneity is reconciled by previous homogenization of an entire sample. The use of sub-samples for MSPD analysis is a smaller scale version of the more classical approach to this problem.

Development of techniques such as MSPD that use smaller sample size, that minimize solvent use and that are amenable to automation is a positive direction for analytical science. The interfacing of such sample preparation and fractionation techniques to immunoassay-based technologies, to micro-devices and enhanced analytical instruments with greater specificity and sensitivity will, in all of its scientific complexity, greatly simplify and speed the task of obtaining essential data.

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