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PURITY AND HEAT OF FUSION DATA FOR ENVIRONMENTAL STANDARDS AS DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Differential scanning calorimetry (DSC) has been applied to 273 environmental standards, including pesticides, herbicides and related compounds. Members of the following chemical classes were analyzed: organophosphorus, organochlorine, phenol, triazine, uracil, phenoxy acid, urea, carboxylic acid, amide, and others including amines, organometallics, esters and heterocycles. Values for the heat of fusion, experimental temperature onset, theoretical temperature onset for 100% pure compound, and percent purity are presented. DSC was found to be a widely applicable method to most classes of organic environmental standards and their metabolites.

INTRODUCTION

DSC has been in use for almost 30 years in the routine analysis of high-purity compounds such as pharmaceuticals and for quality control in the manufacture of plastics [1–4]. The theory and practice of DSC have been reviewed and summarized [5,6]. Calorimetric data for certain pesticides are available [7,8]. Heat of fusion values for environmental standards have generated limited interest in the past and, in general, the manufacturers of commercial chemicals do not necessarily require the stringent control of purity (> 97%) needed for the application of DSC.

The U.S. Environmental Protection Agency (EPA) maintains a repository of pesticides and industrial chemicals to provide high-purity standards and

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reference materials to the scientific community. A number of these reference materials are chemicals regulated under the U.S. EPA Resource Conservation and Recovery Act (RCRA). Many of these compounds and their metabolites are available at sufficiently high purity levels to permit analysis by the DSC technique. The wide variety of complex organic structures can cause non-routine thermal behavior (e.g. decomposition, formation of solid solutions, solid-solid phase transitions, and sublimation) difficult to predict but analytically significant [7,8]. In addition, the use of ΔH_f has been applied as an essential parameter for relating the solubility of solids in a supercritical fluid [9]. DSC provides an accurate measurement of ΔH_f through analysis of the melting curve. Compound purity is determined quantitatively by DSC, and identity is checked qualitatively by melting point.

Even when the purity cannot be determined, it is occasionally possible to gain qualitative evidence by DSC to assist in the identification of the compound. As examples, some compounds decompose rather than melt, and others such as strychnine exhibit a characteristic and unusual melting range. The purpose of this paper is to report the heat of fusion (ΔH_f), melting point, and purity data determined by DSC for 273 environmental standards in support of the EPA Quality Assurance and Quality Control Program. The data are valuable to the EPA both as an analytical reference point and as a source for physical and thermodynamic properties.

EXPERIMENTAL

The DSC system consisted of a Perkin–Elmer DSC-2 coupled to a Perkin–Elmer model 3600 data station using Thermal Analysis Data Station (TADS) software. The instrument was calibrated daily with a high-purity indium standard (99.9999%). The acceptance limits for heat of fusion and temperature onset values were set at 6.8 ± 0.2 cal g^{-1} and 429.79 K, respectively. These control limits were set because of the slow drift in temperature onset over time for this instrument.

All samples were obtained from the Pesticides and Industrial Chemicals Repository maintained by the EPA. Samples were prepared by grinding to a fine powder and weighing 1.5 to 2.0 mg $\pm$ 0.2 mg into an aluminum pan on a Cahn electrobalance. An aluminum cap was placed on the pan and the cap and pan were coldpressed together to form a pellet. Note that gold pans and caps were used for compounds which could react with aluminum, such as organomercury standards. A minimum of two pellets were run for each pesticide. In general, samples were heated at a rate of 2.5 K min^{-1}, over a 20 K range, from an initial temperature of 10 K below the expected temperature onset. The sample weight was selected to produce the best accuracy by providing optimum thermal contact and heat transfer within the sample pan.

TABLE 1

DSC results on environmental standards

Results for each compound analyzed are organized as follows:

(Example)

Compound class — Name (common or trade) — Technical name (Chemical Abstracts) — Chemical Abstracts Service (CAS) No.

AMIDES

Alachlor **15972-60-8**

2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide

99.56	**6050**	**315.88**	**316.71**	**314[13]**

Percent purity exp. — ΔH_f (cal mol^{-1}) — Experimental temperature onset (K) — Theoretical temperature onset (K) — Literature melting point (K)

AMIDES

Alachlor 15972-60-8

2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide

99.56	6050	315.88	316.71	314 [13]

Benzoylprop-Ethyl 22212-55-1

ethyl *N*-benzoyl-*N*-(3,4-dichlorophenyl)-*dl*-alaninate

98.34	6467	341.7	343.27	345 [12]

Daminozide 1596-84-5

N-dimethylaminosuccinamic acid

98.90	8837	431.38	432.39	429 [12]

Desmethyl Diphenamid 954-21-2

N-methyldiphenylacetamide

99.95	7224	439.75	439.87	439 [14]

Desmethyl Formamido Pirimicarb 27218-04-8

99.55	5913	353.08	353.52	353 [14]

Desmethyl Pirimicarb

97.1	10258	429.92	432.56	430 [14]

Dicryl 2164-09-2

N-(3,4-dichlorophenyl)-2-methyl-2-propenamide

99.58	7657	395.47	396.06	401 [15]

Diphenamid 957-51-7

N,*N*-dimethyl-2,2-diphenylbenzeneacetamide

99.85	6078	407.02	407.66	407 [12]

Fluoridamid 47000-92-0

N-[4-methyl-3-[[(trifluoromethyl)sulfonyl]amino]phenyl]acetamide

99.62	9673	455.69	456.31	449 [15]

TABLE 1 (continued)

Mefluidide			53780-34-0	
5′-(trifluoromethanesulphonamide)acet-2′,4-xylidide				
99.94	9001	457.32	457.48	458 [12]
Metalaxyl (Ridomil)			57837-19-1	
methyl *N*-(2-methoxyacetyl)-*N*-(2,6-xylyl)-*dl*-alaninate				
99.53	6324	345.53	346.17	345 [12]
Monalide			7287-36-7	
N-(4-chlorophenyl)-2,2-dimethylpentanamide				
99.71	5571	360.19	360.65	360 [12]
Napropamide			15299-99-7	
N,*N*-diethyl-2-(1-napthyloxy)propionamide				
99.29	5873	345.29	346.97	344 [12]
Naphthalene acetamide			86-86-2	
1-naphthaleneacetamide				
99.66	7845	456.31	457.11	457 [13]
Nitralin			4726-14-1	
4-methylsulphonyl-2,6-dinitro-*N*,*N*-dipropylaniline				
99.83	6703	424.31	424.83	425 [12]
Nitrofen			1836-75-5	
2,4-dichlorophenyl 4-nitrophenyl ether				
99.60	5487	341.96	342.72	343 [12]
Norflurazon			27134-13-2	
4-chloro-5-(methylamino)-2-[3-(trifluoromethyl)phenyl]-3(2*H*)-pyridazinone				
99.65	7816	450.60	451.15	453 [13]
Oryzalin			19044-88-3	
3,5-dinitro-N^4,N^4-dipropylsulphanilamide				
99.52	9198	414.84	415.48	415 [12]
Oryzalin, dimethyl			19044-94-1	
4-(dipropylamino)-*N*,*N*-dimethyl-3,5-dinitrobenzenesulfonamide				
99.62	7785	413.60	414.45	
Oxycarboxin (Plantvax)			5259-88-1	
2,3-dihydro-6-methyl-5-phenylcarbamoyl-1,4-oxathiin-4,4-dioxide				
99.80	6371	401.52	403.24	403 [12]
Oxythioquinox			2439-01-2	
6-methyl-1,3-dithiolo[4,5-*b*]quinoxalin-2-one				
99.81	7150	443.23	443.68	445 [12]
Pendimethalin			40487-42-1	
N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine				
99.87	6020	327.45	327.85	329 [12]
Perfluidone			37924-13-3	
1,1,1-trifluoro-*N*-[2-methyl-4-(phenylsulfonyl)phenyl]methane sulfonamide				
99.57	7597	418.38	419.13	417 [13]

TABLE 1 (continued)

Profluralin			26399-36-0	
N-(cyclopropylmethyl)-2,6-dinitro-*N*-propyl-4-(trifluoromethyl) benzenamine				
97.90	5380	305.84	307.90	306 [13]
Pronamide (Propyzamide)			23950-58-5	
3,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)benzamide				
99.02	6854	428.37	429.68	429 [12]
Propachlor			1918-16-7	
2-chloro-*N*-isopropylacetamide				
99.66	6226	351.32	351.90	350 [12]
Propanil			709-98-8	
3′,4′-dichloropropionanilide				
99.75	4365	363.65	364.30	365 [12]
Propazine			139-40-2	
2-chloro-4,6-bis(isopropylamino)-1,3,5-triazine				
99.92	10006	490.28	490.52	487 [12]
Pyracarbolid			24691-76-7	
3,4-dihydro-6-methyl-2*H*-pyran-5-carboxanilide				
98.55	4591	381.11	381.40	383 [12]
Solan			2307-68-8	
3′-chloro-2-methylvaler-*p*-toluidide				
98.62	3907	353.20	355.94	358 [12]
Thioacetamide			62-55-5	
ethanethioamide				
99.49	4387	385.66	386.42	386 [15]
CARBAMATES				
Aldicarb			116-06-3	
2-methyl-2-(methylthio)propionaldehyde *O*-methylcarbamoyloxime				
99.80	5428	373.99	374.42	373 [12]
Aldicarb Sulfoxide Oxime			14357-44-9	
99.20	6483	381.98	382.58	
Asulam			3337-71-1	
methyl 4-aminophenylsulphonylcarbamate				
98.49	6507	415.60	417.30	417 [12]
Barban			101-27-9	
4-chlorobut-2-ynyl-3-chlorocarbanilate				
97.61	6432	344.11	345.59	348 [12]
Bendiocarb			22781-23-3	
2,3-isopropylidenedioxyphenyl-*N*-methylcarbamate				
99.95	7038	402.62	402.77	402 [13]
Benzadox			5251-93-4	
[(benzoylamino)oxy] acetic acid				
99.60	7519	416.92	417.66	413 [14]

TABLE 1 (continued)

Carbaryl			63-25-2	
1-naphthyl methylcarbamate				
99.80	5858	416.28	416.89	415 [12]
Carbofuran			1563-66-2	
2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate				
99.87	7250	426.24	426.38	426 [12]
Carbofuran, 3-hydroxy-7-phenol			17781-15-6	
2,3-dihydro-2,2-dimethyl-3-hydroxyphenolmethylcarbamate-7-benzofuranol				
98.85	4373	381.54	383.94	381 [14]
Chlorpropham			101-21-3	
isopropyl-3-chlorophenylcarbamate				
99.48	4243	313.81	315.00	315 [12]
CPMC			3942-54-9	
N-methyl-2-chlorophenyl carbamic acid ester				
99.54	5212	362.08	362.70	
Desmedipham			13684-56-5	
ethyl-3-phenylcarbamoyloxyphenylcarbamate				
99.35	7827	394.14	394.81	393 [12]
Dioxacarb			6988-21-2	
2-(1,3-dioxolan-2-yl)phenyl methylcarbamate				
99.61	5692	387.15	388.27	388 [12]
Isoprocarb			2631-40-5	
2-(1-methylethyl)phenyl methylcarbamate				
99.70	6248	369.33	369.94	366 [13]
Meobal (Xylylcarb)			2425-10-7	
3,4-dimethylphenyl methylcarbamate				
99.76	5967	350.81	351.37	349 [13]
Methazole			20354-26-1	
2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione				
99.72	7050	396.34	397.03	397 [13]
Methiocarb			2032-65-7	
4-methylthio-3,5-xylyl methylcarbamate				
99.64	7257	393.79	394.44	391 [13]
Methomyl			16752-77-5	
5-methyl *N*-(methylcarbamoyloxy)thioacetimidate				
99.70	5193	352.67	353.24	352 [13]
Mexacarbate			315-18-4	
4-dimethylamino-3,5-xylyl methylcarbamate				
99.84	4390	361.68	362.06	358 [15]
Oxamyl			23135-22-0	
N,*N*-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide				
99.51	7210	372.23	373.01	373 [13]

TABLE 1 (continued)

Phenmedipham 13684-63-4
methyl 3-*m*-tolylcarbamoyloxyphenylcarbamate
99.47 9470 423.71 424.48 417 [12]

Phosalone 2310-17-0
S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl *O*,*O*-diethyl phosphorodithioate
99.20 7178 319.96 321.56 321 [12]

Promecarb 2631-37-0
5-isopropyl-*m*-tolyl methylcarbamate
99.37 5506 361.26 362.48 360 [12]

Propham 122-42-9
isopropyl phenylcarbamate
99.87 4630 359.47 360.45 360 [12]

Propoxur 114-26-1
2-isopropoxyphenyl methylcarbamate
99.62 5488 362.68 363.62 360 [13]

Pyrolan 87-47-8
3-methyl-1-phenyl-1*H*-pyrazol-5-yl dimethylcarbamate
99.41 5112 324.26 325.17 323 [15]

Swep 1918-18-9
methyl-3,4-dichlorophenylcarbamate
99.06 5542 381.40 382.70 385 [19]

Thiofanox 39196-18-4
3,3-dimethyl-1-(methylthio)butanone *O*-methylcarbamoyloxime
99.52 4739 330.22 331.11 331 [12]

Tranid 15271-41-7
5-chloro-6-[[[(methylamino)carbonyl]oxy]imino]bicyclo{2.2.1} heptane-2-carbonitrile
99.5 6230 431.57 433.40 433 [15]

Vinclozolin 50471-44-8
(*RS*)-3-(3,5-dichlorophenyl)-5-methyl-5-vinyloxazolidine-2,4-dione
99.45 6579 379.09 383.69 381 [12]

CARBOXYLIC ACIDS

Adipic acid 124-04-9
hexanedioic acid
98.99 8774 424.64 426.07 425 [15]

Carboxin 5234-68-4
5,6-dihydro-2-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide
99.44 6877 364.15 364.64 365 [12]

Chloramben 133-90-4
3-amino-2,5-dichlorobenzoic acid
99.92 8943 475.58 475.75 474 [12]

TABLE 1 (continued)

Chlorambucil				305-03-3	
3-[bis(2-chloroethyl)amino]benzenebutanoic acid					
98.89	6973	338.86	340.08		339 [15]
Dacthal monoacid				887-54-7	
methyltetrachloroterephthalic acid ester					
99.72	4038	444.28	444.86		449 [14]
DDA, *p,p'*-				83-05-6	
bis(4-chlorophenyl)acetic acid					
99.20	7567	440.20	441.26		442 [16]
Dicamba				1918-00-9	
3,6-dichloro-2-methoxybenzoic acid					
99.91	5474	386.67	387.23		387 [12]
3,5-Dichlorobenzoic acid				51-36-5	
99.36	5490	459.23	460.51		460 [16]
Dodine				2439-10-3	
1-dodecylguanidinium acetate					
98.71	6359	409.36	410.64		409 [12]
Fenac (chlorfenac)				85-34-7	
2,3,6-trichlorobenzeneacetic acid					
99.33	5362	432.26	433.50		431 [12]
1-Naphthaleneacetic acid				86-87-3	
99.70	5320	405.26	405.95		406 [12]
Stearic acid				57-11-4	
octadecanoic acid					
96.4	13774	340.26	342.30		342 [15]
CHLOROPHENOXY ACIDS					
4-Chlorophenoxy acetic acid				122-88-3	
98.72	8668	429.62	431.48		432 [16]
2,4-D acid				94-75-7	
(2,4-dichlorophenoxy) acetic acid					
99.86	8443	412.48	412.65		413 [12]
2,4-DB acid				94-82-6	
4-(2,4-dichlorophenoxy)butyric acid					
99.92	9183	391.37	391.49		392 [12]
Dichlorprop				120-36-5	
2-(2,4-dichlorophenoxy)propanoic acid					
99.74	7272	389.20	389.64		391 [12]
MCPA acid				94-74-6	
(4-chloro-*o*-tolyloxy) acetic acid					
99.71	7165	392.86	393.44		392 [12]

TABLE 1 (continued)

MCPB acid 94-81-5
4-(4-chloro-2-methylphenoxy)butanoic acid
99.62 7652 373.44 373.86 373 [12]

MCPP acid 93-65-2
2-(4-chloro-2-methylphenoxy)propanoic acid
99.58 6316 366.20 367.30 367 [13]

Silvex acid (fenoprop) 93-72-1
2-(2,4,5-trichlorophenoxy)propionic acid
97.34 9459 450.48 453.81 454 [12]

2,4,5-T acid 93-76-5
(2,4,5-trichlorophenoxy) acetic acid
99.51 9081 428.73 429.51 428 [12]

4-(2,4,5-trichlorophenoxy)butanoic acid
99.32 7236 386.67 388.10 387 [14]

Triclopyr 55335-06-3
3,5,6-trichloro-2-pyridinyloxyacetic acid
99.73 7449 423.27 423.85 423 [13]

ORGANOCHLORINE COMPOUNDS

Acifluorfen (Blazer) 50594-66-6
5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid
99.41 9003 436.63 437.48 430 [15]

Benzoic acid, 2,4,6-trichlorophenyl hydrazide
99.97 7818 439.67 439.93 439 [14]

BHC, gamma (Lindane) 58-89-9
1α,2α,3β,4α,5α,6β-hexachlorocyclohexane
99.88 5290 386.77 387.17 387 [12]

Bifenox 42576-02-3
methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
99.35 6289 358.31 359.27 359 [12]

Bulan 117-26-0
1,1-bis(4-chlorophenyl)-2-nitrobutane
96.7 3682 330.25 337.17 335 [14]

Captafol 2425-06-1
3a,4,7,7a-tetrahydro-2-[(1,1,2,2-tetrachloroethyl)thio]-1*H*-isoindole-1,3(2*H*)-dione
99.88 9613 432.68 432.81 435 [12]

Chloramben-methyl 7286-84-2
3-amino-2,5-dichlorobenzoic acid methyl ester
97.2 3900 331.35 335.09 337 [15]

Chloranil 188-75-2
2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione
99.58 7378 567.11 568.13 565 [12]

TABLE 1 (continued)

Chlordane, alpha			5103-71-9	
1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4-7-methano-1*H*-indene				
99.22	5533	379.88	381.19	377 [12]
Chlorfenson			80-33-1	
4-chlorophenyl 4-chlorobenzenesulphonate				
99.38	5648	360.03	361.00	360 [12]
Chlorobenzilate			510-15-6	
ethyl 4-chloro-α-(4-chlorophenyl)-α-hydroxybenzeneacetate				
99.96	5611	310.35	312.19	310 [12]
Chloroneb			2675-77-6	
1,4-dichloro-2,5-dimethoxybenzene				
99.86	6587	403.83	404.16	406 [13]
Chlorophacinone			3691-35-8	
2-[(4-chlorophenyl)phenylacetyl]-1*H*-indene-1,3(2*H*)-dione				
97.8	8256	416.49	418.14	413 [12]
Chlorothalonil			1897-45-6	
2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile				
99.91	7170	526.40	526.72	524 [12]
Chlorthal-dimethyl (DCPA)			1861-32-1	
dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate				
99.92	7224	431.64	431.87	429 [12]
DDD, *p,p'*-			72-54-8	
1,1'-(2,2-dichloroethylidene)bis(4-chlorobenzene)				
99.31	6528	382.11	383.41	383 [15]
DDE, *o,p'*-			3424-82-6	
1-chloro-2-(2,2-dichloro-1-(4-chlorophenylethenyl)benzene				
98.26	5699	349.76	351.54	351 [14]
DDE, *p,p'*-			72-55-9	
1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene				
99.94	5628	360.44	360.56	363 [14]
DDT, *o,p'*-			789-02-6	
1-chloro-2-(2,2,2-trichloro-1-(4-chlorophenyl)ethyl)benzene				
99.16	5519	345.80	346.97	347 [14]
DDT, *p,p'*-			50-29-3	
1,1'-(2,2,2-trichloroethylidene)bis(4-chlorobenzene)				
99.52	6282	382.05	383.17	382 [12]
Decachlorobiphenyl			2051-24-3	
99.84	9836	580.26	580.66	580 [17]
Dialifor (dialifos)			10311-84-9	
S-[2-chloro-1-(1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)ethyl] *O,O*-diethylphosphorodithioate				
99.16	6040	339.98	341.23	335 [12]

TABLE 1 (continued)

Dicamba, methyl ester			6597-78-0	
methyl 3,6-dichloro-2-methoxybenzoate				
99.71	4420	304.58	305.14	305 [18]
Dichlobenil			1194-65-6	
2,6-dichlorobenzonitrile				
99.97	6254	417.19	417.24	417 [12]
Dichlone			117-80-6	
2,3-dichloro-1,4-napthalenedione				
99.79	6818	468.96	469.56	466 [12]
Dichloran			99-30-9	
2,6-dichloro-4-nitrobenzenamine				
99.94	7047	467.23	467.44	468 [12]
1,2-Dichlorobenzene			95-50-1	
99.16	2789	253.91	255.20	256 [15]
1,4-Dichlorobenzene			106-46-7	
99.98	4256	326.43	326.56	327 [15]
4,4′-Dichlorobenzophenone			85-29-0	
99.68	5176	338.35	338.80	340 [18]
Dicofol, *o,p′*-			10606-46-9	
2-chloro-α-(4-chlorophenyl)-α-(trichloromethyl)benzenemethanol				
99.46	6024	396.26	397.07	397 [14]
Dicofol, *p,p′*-			115-32-2	
4-chloro-α-(4-chlorophenyl)-α-(trichloromethyl)benzenemethanol				
98.96	4675	347.15	348.21	351 [12]
Diclofop, methyl			51338-27-3	
methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propionate				
99.39	6472	314.41	315.26	314 [12]
Diflubenzuron			35367-38-5	
N-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide				
99.20	13382	499.54	501.18	503 [12]
Diuron			330-54-1	
3-(3,4-dichlorophenyl)-1,1-dimethylurea				
99.95	7282	430.53	430.70	431 [12]
Dowco 356			58138-08-2	
2-(3,5-dichlorophenyl)-2-(2,2,2-trichloroethyl)oxirane				
98.13	4430	313.24	315.21	316 [14]
Drazoxolon			5707-69-7	
4-(2-chlorophenylhydraxone)-3-methyl-5-isoxazolone				
99.72	6701	440.42	441.18	440 [12]
Emmi			2597-93-5	
N-ethylmercuri-1,2,3,6-tetrahydro-3,6-endomethano-3,4,5,6,7,7-hexachlorophthalimide				
99.66	6189	464.92	465.69	

TABLE 1 (continued)

Endosulfan I				959-98-8	
6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide					
99.64	2391	379.98	381.27		381 [12]
Endosulfan cyclic sulfate				1031-07-8	
6,7,8,9,10,10-hexachloro-6,9-methano-2,4,3-benzodioxathiepin-3,3-dioxide					
99.60	5176	419.69	420.86		
Ethylan				72-56-0	
1,1′-(2,2-dichloroethylidene)bis(4-ethylbenzene)					
99.56	5578	331.62	332.17		330 [15]
Fenson				80-38-6	
4-chlorophenylbenzenesulfonate					
99.78	5124	332.24	332.42		334 [13]
Fluchloralin				33245-39-5	
N-(2-chloroethyl)-2,6-dinitro-*N*-propyl-4-(trifluoromethyl) benzenamine					
97.8	5516	318.36	320.88		316 [12]
Folpet				133-07-3	
2-[(trichloromethyl)thio]-1*H*-isoindole-1,3(2*H*)-dione					
99.92	8483	454.24	454.52		453 [12]
HCB				118-74-1	
hexachlorobenzene					
99.99	5864	501.11	501.27		504 [12]
Imazalil				35554-44-0	
1-[2-(2,4-dichlorophenyl)-2-(2-propenyloxy)ethyl]-1*H*-imidazole					
99.17	7290	322.61	323.38		323 [19]
Methoxychlor, *o*,*p*′-				30667-99-3	
1-methoxy-2-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)benzene					
97.62	5365	347.58	349.72		349 [14]
Methoxychlor, *p*,*p*′-				72-43-5	
1,1′-(2,2,2-trichloroethylidene)bis[4-methoxybenzene]					
99.69	5707	360.64	361.56		362 [12]
Metoxuron				19937-59-8	
N′-(3-chloro-4-methoxyphenyl)-*N*,*N*-dimethylurea					
99.68	6569	399.16	399.49		399 [12]
Nitrapyrin				1929-82-4	
2-chloro-6-(trichloromethyl)pyridine					
99.69	4656	337.74	339.03		336 [13]
Oxadiazon				19666-30-9	
3-[2,4-dichloro-5-(1-methylethoxy)phenyl]-5-(1,1dimethylethyl)-1,3,4-oxadiazol-2(3*H*)-one					
99.44	6307	360.56	361.25		363 [12]

TABLE 1 (continued)

Oxyfluorfen			42874-03-3	
2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene				
99.39	7186	358.78	359.75	357 [15]
Pentachloraniline			527-20-8	
99.66	4469	505.78	507.06	505 [18]
Procymidone			32809-16-8	
3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]-hexane-2,4-dione				
99.78	7191	438.15	438.40	439 [12]
Prolan			117-27-1	
1,1′-(2-nitropropylidene)bis(4-chlorobenzene)				
97.9	5112	354.26	355.17	354 [15]
Pyrazon (chloridazon)			1698-60-8	
5-amino-4-chloro-2-phenyl-3(2*H*)-pyridazinone				
99.90	6394	479.16	479.38	479 [12]
Quintozene (PCNB)			82-68-8	
pentachloronitrobenzene				
99.95	4233	417.47	417.58	417 [12]
Silvex, methyl ester			4841-20-7	
methyl 2-(2,4,5-trichlorophenoxy)propionate				
99.40	7636	360.62	361.16	362 [14]
2,4,5-T methyl ester			1928-37-6	
(2,4,5-trichlorophenoxy)acetic acid methyl ester				
99.65	7281	361.89	363.35	363 [14]
Tecnazene			117-18-0	
1,2,4,5-tetrachloro-3-nitrobenzene				
99.87	4650	373.22	373.55	372 [12]
Tetradifon			116-29-0	
1,2,4-trichloro-5-[(4-chlorophenyl)sulfonyl]benzene				
99.93	6917	419.82	420.09	421 [12]
1,2,3-Trichlorobenzene			87-61-6	
99.48	4124	322.91	323.75	326 [15]
1,3,5-Trichlorobenzene			108-70-3	
99.81	4110	333.87	334.45	336 [15]
ORGANOPHOSPHORUS COMPOUNDS				
Acephate			30560-19-1	
O,S-dimethylacetylphosphoramidothioate				
98.86	4928	363.92	365.10	366 [12]
Azinphos ethyl			2642-71-9	
S-(3,4-dihydro-4-oxobenzo[*d*]-[1,2,3]-triazin-3-ylmethyl) *O,O*-diethylphosphorodithioate				
98.31	6027	322.16	324.44	326 [12]

TABLE 1 (continued)

Azinphos methyl 86-50-0
S-(3,4-dihydro-4-oxobenzo[*d*]-[1,2,3]-triazin-3-ylmethyl) *O*,*O*-dimethylphosphorodithioate
99.58 6635 345.33 346.28 346 [12]

Bensulide 741-58-2
O,*O*-diisopropyl *S*-2-phenylsulphonylaminoethyl phosphorodithioate
98.76 7317 310.40 311.57 308 [12]

Bromophos 2104-96-3
O-(4-bromo-2,5-dichlorophenyl) *O*,*O*-dimethyl phosphorothioate
99.36 7444 325.33 325.89 327 [12]

Chlorpyrifos 2921-88-2
O,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate
99.93 5862 315.00 315.25 315 [12]

Chlorpyrifos, methyl 5598-13-0
O,*O*-dimethyl *O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate
99.72 6194 318.70 319.16 319 [12]

Chlorpyrifos, oxygen analog 5598-15-2
diethyl-3,5,6-trichloro-2-pyridinylphosphoric acid ester
99.07 3732 312.54 314.29

Crufomate 299-86-5
methylphosphoramidic acid 2-chloro-4-(1,1-dimethylethyl)phenyl methyl ester
99.23 5253 332.04 333.29 333 [15]

Cyclophosphamide 50-18-0
2-[bis(2-chloroethyl)amino]tetrahydro-2*H*-1,3,2-oxazophosphorine-2-oxide
99.30 7918 322.60 323.52 318 [15]

Cythioate 115-93-5
O,*O*-dimethyl *O*-(4-aminosulfonylphenyl)phosphorothioate
98.86 6264 344.24 345.67 346 [13]

Dimethoate 60-51-5
O,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate
99.29 4898 320.95 321.22 324 [12]

Ditalimfos 5131-24-8
O,*O*-diethyl phthalimidophosphonothioate
99.44 5511 357.27 357.88 357 [12]

EPN 2104-64-5
O-ethyl *O*-(4-nitrophenyl)phenylphosphonothioate
98.81 5988 308.24 309.59 309 [13]

Ethephon 16672-87-0
2-chloroethyl phosphonic acid
98.75 3535 347.92 349.87 348 [12]

TABLE 1 (continued)

Famphur			52-85-7	
O-[4-[(dimethylamino)sulfonyl]phenyl] *O*,*O*-dimethyl-phosphorothioate				
98.08	6333	326.80	328.72	327 [13]
Leptophos			21609-90-5	
O-(4-bromo-2,5-dichlorophenyl) *O*-methyl phenylphosphonothioate				
98.44	7494	345.64	347.14	345 [14]
Methamidophos			10265-92-6	
O,*S*-dimethyl phosphoramidothioate				
97.5	3188	316.84	319.85	318 [12]
Methidathion			950-37-8	
S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl *O*,*O*-dimethyl phosphorodithioate				
99.60	6821	315.05	315.61	313 [13]
Monocrotophos			6923-22-4	
dimethyl (*E*)-1-methyl-2-methylcarbamoylvinyl phosphate				
99.32	5345	326.93	328.12	328 [13]
Parathion, ethyl			56-38-2	
O,*O*-diethyl *O*-4-nitrophenyl phosphorothioate				
99.81	3758	278.06	278.53	279 [12]
Parathion, methyl			298-00-0	
O,*O*-dimethyl *O*-4-nitrophenyl phosphorothioate				
99.22	4797	308.24	309.24	309 [12]
Phosmet			732-11-6	
O-*O*-dimethyl *S*-phthalimidomethyl phosphorodithioate				
99.52	6444	343.19	344.00	345 [12]
Pyrazophos			13457-18-6	
O-6-ethoxycarbonyl-5-methylpyrazolo[1,5-*a*]pyrimidin-2-yl *O*,*O*-diethylphosphorothioate				
98.96	6530	324.41	325.23	324 [12]
Quinalphos			13593-03-8	
O,*O*-diethyl *O*-quinoxalin-2-yl phosphorothioate				
99.70	6070	304.14	304.48	304 [12]
Ronnel			299-84-3	
O,*O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate				
98.06	4526	312.96	314.99	314 [12]
Salithion			3811-49-2	
2-methoxy-4*H*-1,3,2-benzodioxaphosphorin 2-sulfide				
98.79	4044	327.86	329.51	327 [13]
Temephos			3383-96-8	
O,*O*,*O*′,*O*′-tetramethyl *O*,*O*′-thiodi-*p*-phenylene bis(phosphorothioate)				
98.90	7894	303.17	304.42	304 [12]

TABLE 1 (continued)

Tetrachlorvinphos			22248-79-9	
(*Z*)-2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate				
99.68	8440	369.16	369.65	370 [12]
Trichlorfon			52-68-6	
dimethyl (2,2,2-trichloro-1-hydroxyethyl)phosphonate				
98.76	4868	350.96	355.36	356 [12]
Zytron			299-85-4	
O-(2,4-dichlorophenyl) *O*-methyl-(1-methylethyl) phosphoramidothioate				
99.42	6992	321.50	322.39	325 [15]
PHENOLS				
4-Bromo-2,5-dichlorophenol			1940-42-7	
99.60	5285	343.36	343.97	340 [17]
Bromoxynil			1689-84-5	
3,5-dibromo-4-hydroxybenzonitrile				
99.88	7655	463.90	464.20	467 [12]
Carbofuran, 3-keto phenol			11781-16-7	
2,3-dihydro-2,2-dimethyl-7-benzofuranol-3-one				
99.99	5209	440.63	441.55	
Diaphene			87-10-5	
3,5-dibromo-*N*-(4-bromophenyl)-2-hydroxybenzamide				
99.32	6852	497.70	499.58	500 [15]
Dicamba, 5-hydroxy			7600-50-2	
3,6-dichloro-5-hydroxy-2-methoxybenzoic acid				
99.68	6926	409.82	410.35	410 [14]
3,4-Dichlorophenol			95-77-2	
99.58	4705	337.44	338.11	339 [16]
Diethylstilbestrol			56-53-1	
4,4′-(1,2-diethyl-1,2-ethenediyl)bisphenol				
98.91	7591	443.76	445.56	445 [15]
Dinoseb			88-85-7	
2-*sec*-butyl-4,6-dinitrophenol				
97.2	5213	313.65	316.42	315 [12]
DNOC			534-52-1	
2-methyl-4,6-dinitrophenol				
99.56	4640	359.21	360.25	359 [12]
Ethirimol			23947-60-6	
5-butyl-2-ethylamino-6-methylpyrimidin-4-ol				
99.21	4856	432.44	434.35	433 [12]
Hexachlorophene			70-30-4	
2,2′-methylenebis[3,4,6-trichlorophenol]				
99.54	7949	437.51	438.14	438 [15]

TABLE 1 (continued)

Ioxynil			1689-83-4	
4-hydroxy-3,5-diiodobenzonitrile				
99.59	8038	482.92	488.91	486 [12]
1-Napthol			90-15-3	
99.56	5338	367.17	368.02	368 [16]
2-Nitrophenol			88-75-5	
98.73	4280	318.64	319.75	318 [15]
4-Nitrophenol			100-02-7	
99.92	4508	386.14	386.28	386 [15]
PCP			87-86-5	
pentachlorophenol				
99.83	3689	462.99	463.84	463 [15]
2-Phenylphenol			90-43-7	
(1,1′-biphenyl)-2-ol				
99.80	3218	330.78	331.20	330 [12]
2,4,5-Trichlorophenol			95-95-4	
99.52	5160	340.29	341.20	340 [15]
3,5,6-Trichloro-2-pyridinol			1970-40-7	
99.98	6165	448.04	447.94	449 [14]
TRIAZINES				
Anilazine			101-05-3	
4,6-dichloro-*N*-(2-chlorophenyl)-1,3,5-triazin-2-amine				
98.29	7523	430.95	432.48	432 [12]
Atrazine			1912-24-9	
6-chloro-*N*-ethyl-*N′*-(1-methylethyl)-1,3,5-triazine-2,4-diamine				
99.13	9119	449.66	450.49	448 [12]
Cyanazine			21725-46-2	
2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methyl-propanenitrile				
99.52	10028	437.91	438.74	441 [12]
Cyprazine			22936-86-3	
6-chloro-*N*-cyclopropyl-*N′*-(1-methylethyl)-1,3,5-triazine-2,4-diamine				
97.5	6874	441.56	443.54	441 [14]
Dipropetryn			4147-51-7	
6-(ethylthio)-*N*, *N′*-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine				
99.52	5722	377.66	378.13	379 [13]

TABLE 1 (continued)

Hexazinone			51235-04-2	
3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione				
99.69	4866	389.56	390.35	390 [12]
Procyazine			32889-48-8	
2-((4-chloro-6-(cyclopropylamino)-1,3,5-triazin-2-yl)amino-2-methylpropanenitrile				
97.2	5381	438.54	442.31	441 [14]
Prometon			1610-18-0	
6-methoxy-*N*,*N*′-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine				
99.64	5062	363.52	364.35	364 [12]
Prometryn			7287-19-6	
N,*N*′-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine				
99.69	5849	392.85	393.33	393 [12]
Simazine			122-34-9	
6-chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine				
99.81	11317	502.48	502.93	500 [12]
Terbuthylazine			5915-41-3	
6-chloro-*N*-(1,1-dimethylethyl)-*N*′-ethyl-1,3,5-triazine-2,4-diamine				
99.52	8024	448.58	449.23	450 [12]
Terbutryn			886-50-0	
N-(1,1-dimethylethyl)-*N*′-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine				
99.58	5120	375.89	376.98	377 [12]
URACILS				
Bromacil			314-40-9	
5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1*H*,3*H*)-pyrimidinedione				
99.32	5263	428.26	430.92	431 [12]
Lenacil			2164-08-1	
3-cyclohexyl-6,7-dihydro-1*H*-cyclopentapyrimidine-2,4(3*H*,5*H*)-dione				
99.68	10112	584.26	584.55	588 [12]
Terbacil			4902-51-2	
5-chloro-3-(1,1-dimethylethyl)-6-methyl-2,4(1*H*,3*H*)-pyrimidinedione				
99.78	2989	448.04	449.48	450 [12]
UREAS				
Chlorbromuron			13360-45-7	
3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea				
99.44	6344	369.76	370.66	370 [12]
1-(*o*-Chlorophenyl)thiourea			5344-82-1	
98.08	5328	413.53	416.44	416 [16]

TABLE 1 (continued)

Chloroxuron			1982-47-4	
3-[4-(4-chlorophenoxy)phenyl]-1,1-dimethylurea				
99.92	8333	425.79	425.83	425 [12]
Fenuron			101-42-8	
1,1-dimethyl-3-phenylurea				
99.26	5452	404.77	406.38	406 [13]
Fluometuron			2164-17-2	
N,*N*-dimethyl-*N'*-[3-(trifluoromethyl)phenyl]urea				
99.76	7127	434.06	434.80	436 [13]
Isoproturon			34123-59-6	
N,*N*-dimethyl-*N'*-[4-(1-methylethyl)phenyl]urea				
99.84	8096	430.44	430.81	426 [12]
Linuron			330-55-2	
N'-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea				
99.28	6347	365.70	366.76	366 [12]
Metobromuron			3060-89-7	
N'-(4-bromophenyl)-*N*-methoxy-*N*-methylurea				
99.64	5842	368.25	368.88	369 [12]
Monolinuron			1746-81-2	
N'-(4-chlorophenyl)-*N*-methoxy-*N*-methylurea				
99.61	5387	353.38	353.91	353 [12]
Monuron			150-68-5	
3-(4-chlorophenyl)-1,1-dimethylurea				
99.88	7040	447.56	447.88	447 [12]
Monuron, TCA			140-41-0	
N'-(4-chlorophenyl)-*N*,*N*-dimethyltrichloroacetateurea				
98.24	6349	353.99	355.50	354 [13]
Neburon			555-37-3	
N-butyl-*N'*-(3,4-dichlorophenyl)-*N*-methylurea				
99.08	6508	374.25	374.86	375 [12]
Norea			18530-56-8	
N,*N*-dimethyl-*N'*-(octahydro-4,7-methano-1*H*-inden-5-yl)urea				
97.2	5197	436.53	441.87	449 [15]
Tebuthiuron			34014-18-1	
N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N*,*N'*-dimethylurea				
99.28	7045	435.27	436.61	437 [12]
Thiourea			62-56-6	
99.19	3446	445.52	448.05	449 [15]
OTHERS				
Acenaphthylene			83-32-9	
1,8-ethylenenapthalene				
99.24	2620	362.01	364.02	366 [15]

TABLE 1 (continued)

Amdro				67485-29-4	
3-(4-(trifluoromethyl)phenyl)-1-(2-(4-(trifluoromethyl)phenyl)-ethenyl)-2-propenylidene)hydrazonetetrahydro-5,5-dimethyl-2(1*H*)-pyrimidinone					
98.60	8492	463.82	466.45		464 [15]
2-Aminobutane hydrochloride				10049-60-2	
99.69	2405	421.27	422.59		421 [14]
Amitrole				61-82-5	
1*H*-1,2,4-triazol-3-amine					
99.70	5242	428.24	429.28		430 [12]
Ancymidol				12771-68-5	
α-cyclopropyl-α-(4-methoxyphenyl)-5-pyrimidinemethanol					
99.14	6365	383.13	384.57		384 [12]
Anthraquinone				84-65-1	
9,10-anthracenedione					
99.60	8310	556.92	557.96		559 [12]
Antor (diethatyl-ethyl)				38727-55-8	
N-(chloroacetyl)-*N*-(2,6-diethylphenyl)glycine ethyl ester					
99.52	5698	318.01	319.00		322 [19]
Avitrol				504-24-5	
4-aminopyridine					
99.30	4796	429.94	431.98		433 [16]
Azobenzene				103-33-3	
Diphenyldiazine					
99.70	4981	338.76	339.99		341 [15]
Bayleton				43121-43-3	
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*,1,2,4-triazol-1-yl)-2-butanone					
98.33	5465	351.43	353.62		355 [12]
Benefin (Benfluralin)				1861-40-1	
N-butyl-*N*-ethyl-2,6-dinitro-4-trifluoromethylaniline					
99.80	8723	338.44	338.72		338 [13]
Bentazon				25057-89-0	
3-(1-methylethyl)-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide					
99.70	5202	412.47	412.81		412 [12]
Benzyl benzoate				120-51-4	
phenylmethylbenzoate					
98.30	4886	293.05	294.99		294 [15]
Binapacryl				485-31-4	
2-*sec*-butyl-4,6-dinitrophenyl 3-methylcrotonate					
98.10	4516	341.27	343.76		341 [12]

TABLE 1 (continued)

Bromopropylate			18181-80-1	
isopropyl 4,4′-dibromobenzilate				
99.05	5868	348.02	349.12	350 [13]
Bromoxynil octanoate			1689-99-2	
3,5-dibromo-4-hydroxybenzonitrile octanoyl ester				
98.95	6331	318.25	319.27	319 [12]
Buthidazole			55511-98-3	
3-(5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)-4-hydroxy-1-methyl-2-imidazolidinone				
98.76	6085	408.95	410.42	407 [13]
Butralin			33629-47-9	
4-(1,1-dimethylethyl)-*N*-(1-methylpropyl)-2,6-dinitrobenzenamine				
98.59	4981	338.76	332.47	333 [13]
Cacodylic acid (dimethyl arsinic acid) 75-60-5				
hydroxydimethylarsine oxide				
99.06	5845	470.78	472.58	471 [13]
d-Camphor			464-49-3	
1,7,7-trimethylbicyclo[2.2.1]heptan-2-one				
99.74	3760	462.34	463.38	453 [15]
Chlordimeform			6164-98-3	
N′-(4-chloro-2-methylphenyl)-*N*, *N*-dimethylmethanimidamide				
99.87	4927	305.27	305.76	305 [12]
Chromium trioxide			1333-82-0	
99.69	2877	468.89	470.44	470 [15]
Coumafuryl			117-52-2	
3-[1-(2-furanyl)-3-oxobutyl]-4-hydroxy-2*H*-1-benzopyran-2-one				
96.3	8098	391.75	395.26	397 [12]
Deltamethrin			52918-00-5	
(*S*)-α-cyano-3-phenoxybenzyl(1*R*)-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate				
99.51	9729	372.85	373.50	374 [13]
Difenzoquat			43222-48-6	
1,2-dimethyl-3,5-diphenyl-1*H*-pyrazolium methyl sulfate				
99.10	7114	430.14	431.63	433 [13]
Dinitramine			2091-05-2	
N^3, N^3-diethyl-2,4-dinitro-6-(trifluoromethyl)-1,3-benzenediamine				
99.84	6963	372.11	372.46	372 [13]
Diphenylamine			122-39-4	
N-phenylbenzeneamine				
99.64	4407	325.62	326.40	326 [15]
Ethofumesate			26225-79-6	
±2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulfonate				
98.67	6273	344.08	345.62	345 [12]

TABLE 1 (continued)

Fenbutatin oxide				13356-08-6	
hexakis(2-methyl-2-phenylpropyl)distannoxane					
97.94	17163	417.70	418.99		412 [12]
Fentin acetate				900-95-8	
(acetyloxy)triphenylstannane					
99.44	10020	397.61	398.33		398 [12]
Fentin hydroxide				76-87-9	
hydroxytriphenylstannane					
99.75	2442	388.98	390.88		391 [12]
Fluorodifen				15457-05-3	
2-nitro-1-(4-nitrophenoxy)-4-(trifluoromethyl)benzene					
99.44	4407	364.52	364.88		367 [13]
Flurecol, butyl ester				2314-09-2	
butyl 9-hydroxy-9*H*-fluorene-9-carboxylate					
99.45	6108	343.83	344.68		344 [12]
Metribuzin				21087-64-9	
4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one					
99.82	4301	399.35	399.94		400 [12]
Naphthalic anhydride (Protect)				81-84-5	
1*H*,3*H*-napththo(1,8*cd*)pyran-1,3-dione					
96.7	5574	542.34	545.7		547 [13]
Phthalic anhydride				85-44-9	
1,3-isobenzofurandione					
99.78	5519	403.29	403.73		404 [15]
Phenanthrene				85-01-8	
99.66	3799	372.06	372.74		373 [15]
Phenothiazine				92-82-2	
10*H*-phenothiazine					
99.91	6433	458.19	458.39		458 [15]
Phenyl ether				101-84-8	
phenoxybenzene					
99.58	3862	299.78	300.58		301 [15]
Pindone				83-26-1	
2-pivaloylindan-1,3-dione					
99.13	6211	381.52	382.88		382 [12]
1,3-Propane sulfone				1120-71-4	
99.27	2381	302.22	304.33		304 [16]
Resmethrin				10453-86-8	
5-benzyl-3-furylmethyl (1*RS*)-*cis,trans*-chrysanthemate					
99.22	9672	330.37	330.62		321 [12, mixture]

TABLE 1 (continued)

Rotenone				83-79-4	
[2*R*-(2α,6aα,12aα)]-1,2,12,12a-tetrahydro-8,9-dimethoxy-2-(1-methylethenyl) [1] benzopyrano [3,4-*b*]furo[2,3-*h*][1]benzopyran-6(6*aH*)-one					
98.38	8518	437.86	438.20		436 [13]
Triadimenol (Baytan)				55219-65-3	
β(4-chlorophenoxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole--1-ethanol					
97.9	5849	377.83	380.99		385 [12]
Tri-allate				2303-17-5	
S-2,3,3-trichloroallyl diisopropylthiocarbamate					
99.14	6480	306.30	307.19		303 [12]
Tricyclazole				41814-78-2	
5-methyl-1,2,4-triazolo[3,4-*b*]-benzothiazole					
99.92	5753	460.22	460.49		460 [13]
Trifluralin				1582-09-8	
2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)benzenamine					
99.80	5335	321.35	322.19		322 [12]

The scan rate determination was a compromise between accuracy and analysis time [10]. If the sample could be resolidified, it was remelted and the remelt results reported. Results for 273 compounds are summarized in Table 1. An example endotherm is shown in Fig. 1, and a van't Hoff plot in Fig. 2.

RESULTS AND DISCUSSION

Experimentally determined temperature onset (Exp. T), heat of fusion (ΔH_f), and purity (% purity) determinations by DSC are presented in Table 1. Average values shown were calculated from two or more determinations. Theoretical temperature onset (Theo. T) for 100% pure compound, and literature melting points (Lit. m.p.) are included for comparison and usually agreed within 3 K. Compounds are grouped according to class and ordered alphabetically by common name. Many of the compounds are multifunctional, so the grouping by class cannot be completely unambiguous. The common name may be a trivial chemical name, a familiar trade name, or an abbreviation. Because most of these compounds are structurally complex, Chemical Abstracts Service (CAS) and International Union of Pure and Applied Chemistry (IUPAC) names are seldom used except for verification. The CAS names and CAS registration numbers are provided in Table 1 for clarity and structural verification.

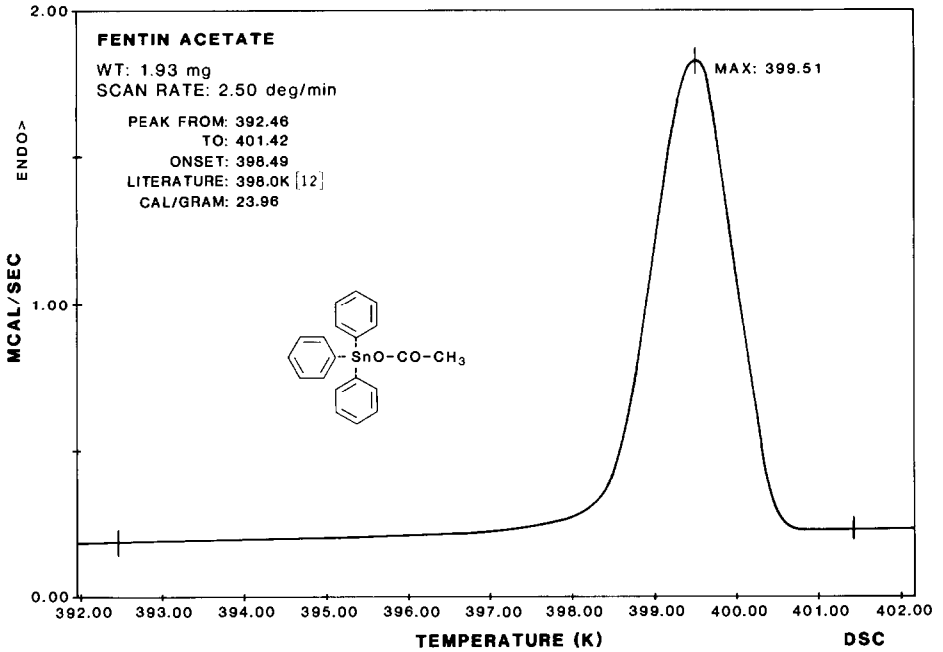

Fig. 1. DSC thermogram of fentin acetate.

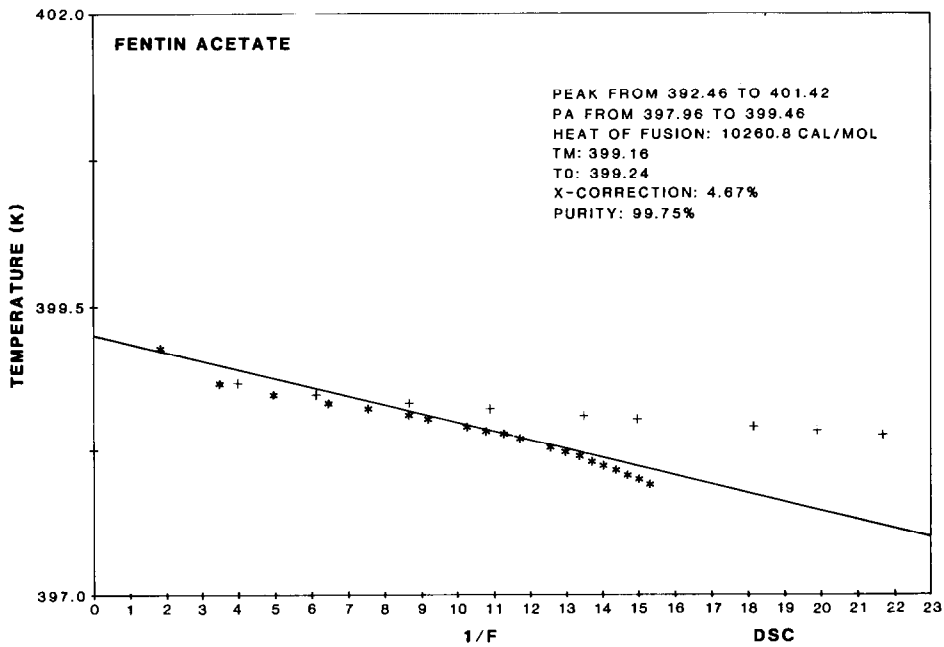

Fig. 2. van't Hoff plot of fentin acetate.

Temperature onset values were obtained from thermograms by taking the slope of the melting curve at the inflection point and extrapolating to the baseline. Most compounds reported in this study show a temperature onset very close to the literature melting point. However, a few compounds were observed to exhibit melting point depression. Possible reasons for the discrepancies may be related to the differences in the purity levels of compounds analyzed (see Fig. 3 and Table 2), or to the accuracy of the method used to determine literature values. It has long been recognized that compounds prone to sublimation should be analyzed in a sealed tube; such was the case in literature references for camphor and chloranil. Traditional literature melting points or ranges have been measured by observing the temperature at which melting begins and the temperature range over which the sample melts. Weaknesses in the traditional open and closed capillary tube methods include the possibility of inaccurate thermometers, melting point variation with ambient pressure, and hygroscopic variability.

Other identification techniques, such as mass spectrometry (MS), infrared (IR), or nuclear magnetic resonance (NMR) spectrometry, and/or elemental analysis were also used routinely for these compounds. Generally, two complementary techniques were applied, one such as DSC primarily to ascertain purity, and the other, such as MS, primarily to verify identity.

Some compounds exhibited anomalous behavior such as multiple peaks and unusual curve shapes resulting in failure of the DSC technique for certification of purity. Some considerations which may cause anomalous

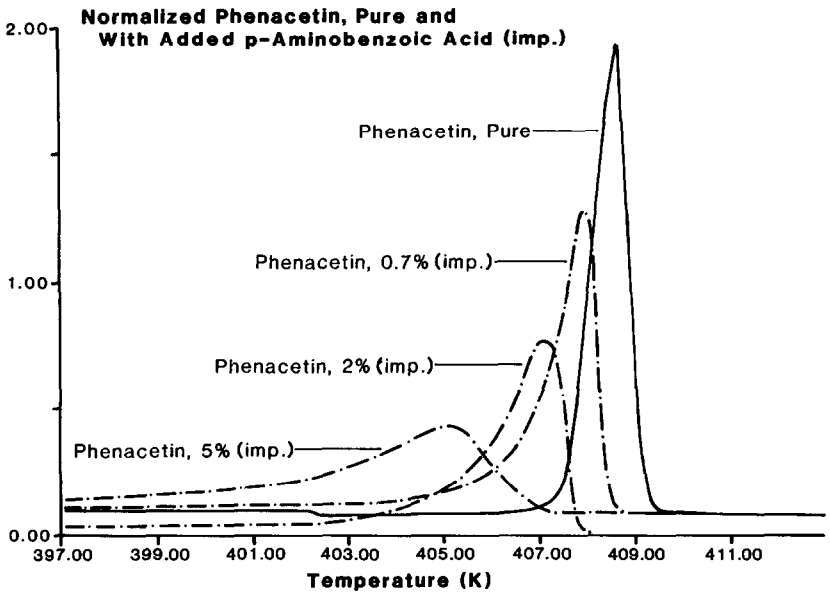

Fig. 3. Effect of added impurity on DSC thermogram.

TABLE 2

National Institute of Standards and Technology, Standard Reference Material 1514 thermal analysis purity set. *p*-Aminobenzoic acid impurity in phenacetin

p-Aminobenzoic acid (mol%) Nominal	Certified
0.0	0.0
0.7	0.69 ± 0.07
2.0	1.91 ± 0.12
5.0	5.02 ± 0.46
Phenacetin calculated (from NIST)	**Phenacetin DSC result (experimental)**
99.9 ± 0.2	99.32
99.2 ± 0.2	99.02
98.0 ± 0.2	98.08
94.9 ± 0.5	96.10

behavior are: (1) the presence of impurities which are immiscible in the liquid phase and melt at their own characteristic melting point; (2) solid–solid phase transitions such as a change in crystal structure; (3) a crystal acquiring rotational freedom at a lower temperature than that required for translational freedom [7,8,11]; (4) solids having significant vapor pressure; and (5) sublimation such as is observed for camphor when melted in an open capillary tube.

The presence of impurities can affect the thermogram in several ways. Multiple peaks and distorted curves are the most common indication of impurities. The assumption that an impurity is insoluble in the solid phase is not valid if the molecule can fit into the crystal lattice of the solid phase without causing distortion. This situation occurs in those cases where an impurity is similar in size to the principal component. For example, when hexachlorobenzene is added to pentachloronitrobenzene, the purity determination by DSC is falsely high [7]. Performing a quantitative analysis by another method helps to insure that the purity reported is a true value.

When compounds have more than one crystalline form, they can first be heated above the melting point of the lower melting form in an attempt to convert the lower melting crystals to the higher melting crystal form before a purity determination is performed. Bentazon, chlorfenson, and monuron are three compounds reported in this study which exhibit dimorphic behavior but could be successfully analyzed for purity by DSC.

Compounds having a low entropy of fusion ($\Delta S_f < 5$ cal mol^{-1} K^{-1}) exhibit rotational motion in the solid form and need only to obtain translational motion on melting [8]. The ΔS_f value can be calculated from DSC data ($\Delta S_f = \Delta H_f / T_0$). Such compounds may readily form solid solutions

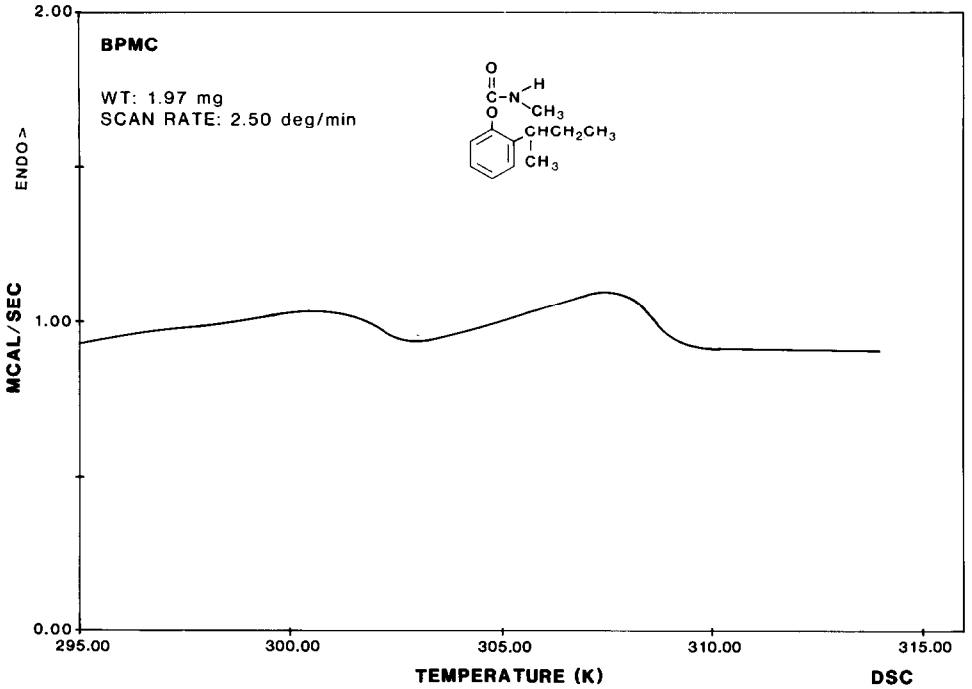

Fig. 4. DSC thermogram of BPMC.

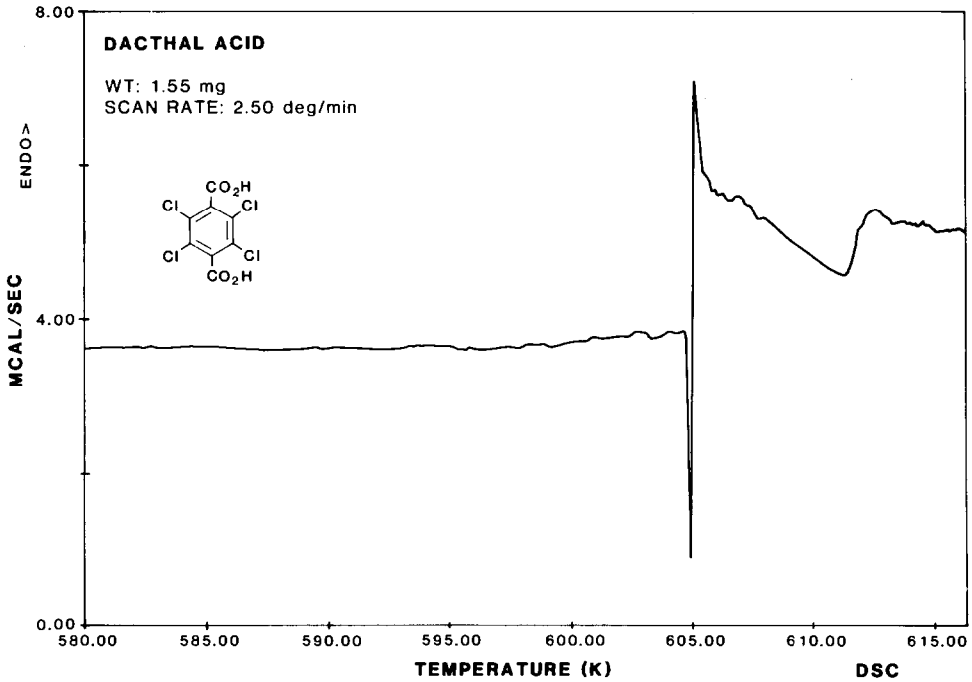

Fig. 5. DSC thermogram of dacthal acid.

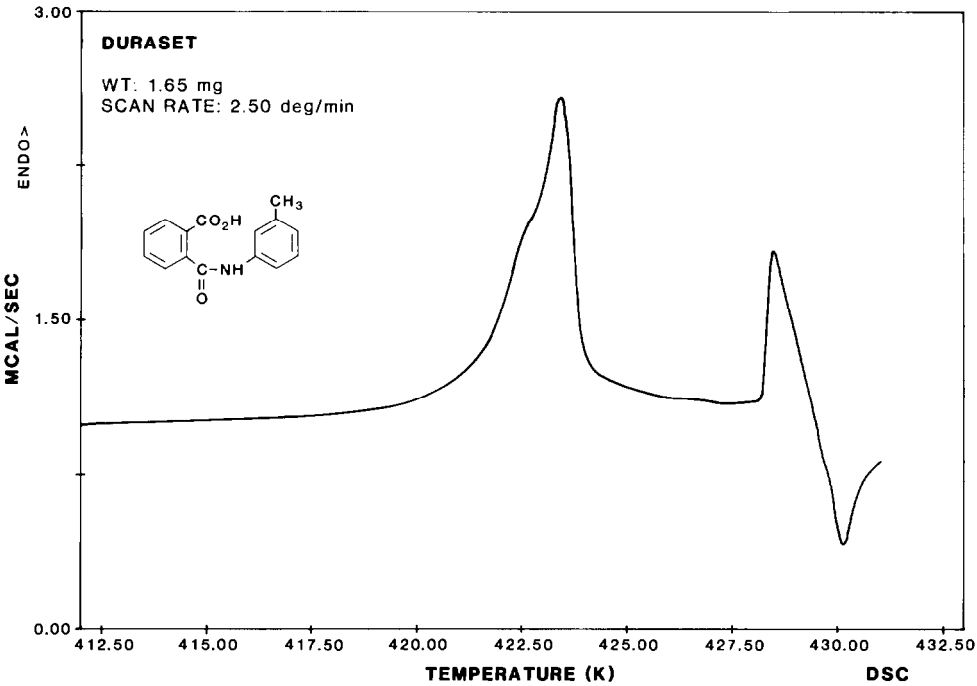

Fig. 6. DSC thermogram of duraset.

with impurities. Purity values determined for compounds with low entropies of fusion are likely to be suspect (e.g. results for ametryn are not included in Table 1). Additionally, acenaphthylene, 2-aminobutane hydrochloride, chromium trioxide, endosulfan I, fentin hydroxide, pentachlorophenol, 1,3-propane sulfone, terbacil and thiourea all had $\Delta S_f < 8$ cal mol^{-1} K^{-1} and thus may have the potential of forming solid solutions with impurities, although they were included in Table 1. Experimental purity values could be higher than the true purity for these compounds.

Most compounds exhibited normal behavior. However, certain chemical classes exhibited noteworthy characteristics under DSC. Eight classes are discussed below.

(1) Amides

Compounds of this class usually can be analyzed by DSC if no other functional groups are present in the molecule, such as phenolic hydroxyl or carboxyl, which could react with the amide.

(2) Carbamates and ureas

Compounds decomposing at or near their melting point are unsuitable for DSC. *N*-methylcarbamates, ureas, and thioureas tend to decompose readily.

Thiophanate melts, but has a decomposition temperature just above its melting point. Only one *N*-methylcarbamate tested, 2-chlorophenyl-*N*-methylcarbamate (CPMC), provided an acceptable thermogram. Another *N*-methylcarbamate, 2-(*sec*-butyl)phenyl-*N*-methylcarbamate (BPMC), showed two small but distinct endotherms near its melting point (Fig. 4) and was not included in Table 1. The small amount of energy absorbed indicates the compound has already gained rotational energy, while the two peaks in the graph are probably caused either by the BPMC being polymorphic or by two separate compounds being present.

(3) Carboxylic acids

Thirteen compounds of this class were analyzed successfully, having melting points ranging from 338 K to 475 K. If the melting point of the acid is higher, decomposition begins to occur. Higher-melting acids, such as dacthal diacid, which melts at about 605 K, often showed some decomposition, as evidenced by a sharp exotherm followed immediately by a complex and nonreproducible endotherm (Fig. 5). They were not included in Table 1.

Duraset, which contains *ortho*-carboxylic acid and amide groups, displayed evidence of reactivity. After melting at 422 K, a clear exotherm was seen at 428 K, possibly due to the functional groups reacting with one another (Fig. 6). Naptalam sodium salt also has an amide group ortho to the carboxylic acid salt and showed an exotherm immediately before the endotherm. These compounds were not included in Table 1.

(4) Organophosphorus compounds

As was observed by Plato [8], organophosphorus compounds are difficult to resolidify under DSC conditions. Thus, results reported for many of these compounds are from initial melts only. However, a small amount of decomposition at the melting point may not be apparent until a second melt is performed. Some samples of dialifor, a phosphorodithioate, partially decomposed during the initial melt. The decomposition appeared on the remelt thermogram in the form of a distinct shoulder on the leading edge of the melting peak. The decomposition was not readily visible on the initial thermogram.

(5) Phenols

Most of the compounds of this class were successfully analyzed by DSC. Failures occurred when other functional groups were present and could react with phenolic groups. Phenols with unusual thermograms included niclosamide with an amide group *ortho* to the phenolic group, and 3,6-dichlorosalicylic acid with a carboxylic acid group *ortho* to the phenolic group. The

niclosamide thermogram (Fig. 7) showed a small heat of fusion with an abrupt leading edge in the melting peak and a long trailing edge. These two compounds were not included in Table 1.

(6) Triazines

Some pesticide samples of the 1,3,5-triazine class show an unusual characteristic thermogram shape (see Fig. 8, atrazine). Presumably, ametryn was non-ideal because the experimentally determined entropy of fusion was less than 5 cal mol^{-1} K^{-1}. The leading edge of the melting curve showed an irregularity containing two or three bumps. Remelting the sample greatly reduced or eliminated this behavior. If the sample had been rapidly crystallized from solution, the s-triazine crystals might have internal mechanical (crystal lattice) stress, which appeared in the initial melting curve as the bumps noted above.

(7) Ethers

Several ethers were determined successfully, such as methoxychlor, Silvex, 2-methyl-2-chlorophenoxyacetic acid (MCPA), 2-methyl-4-chlorophenoxy-

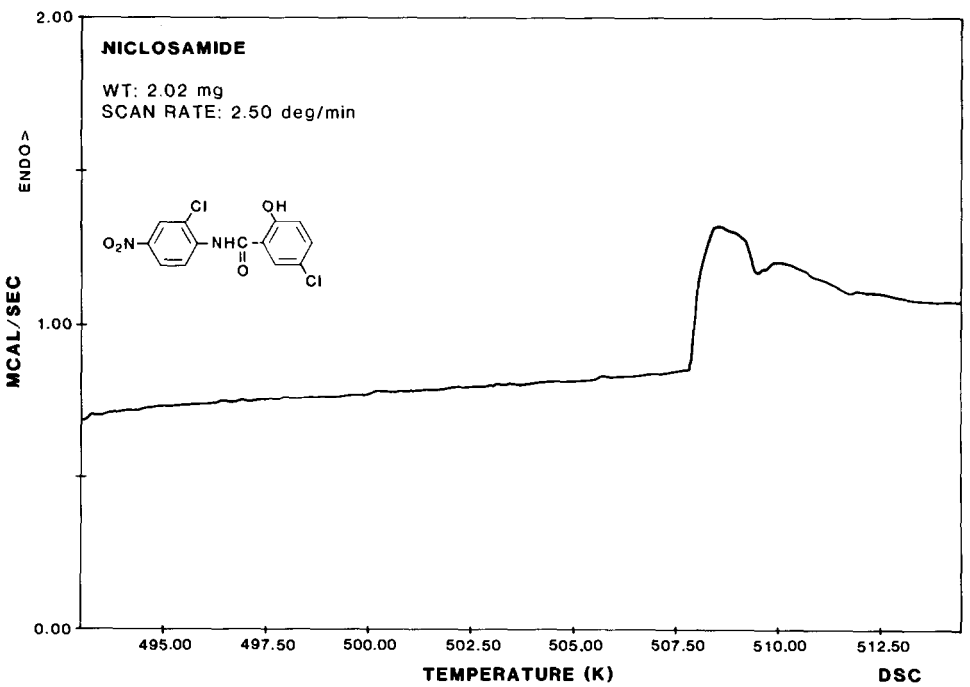

Fig. 7. DSC thermogram of niclosamide.

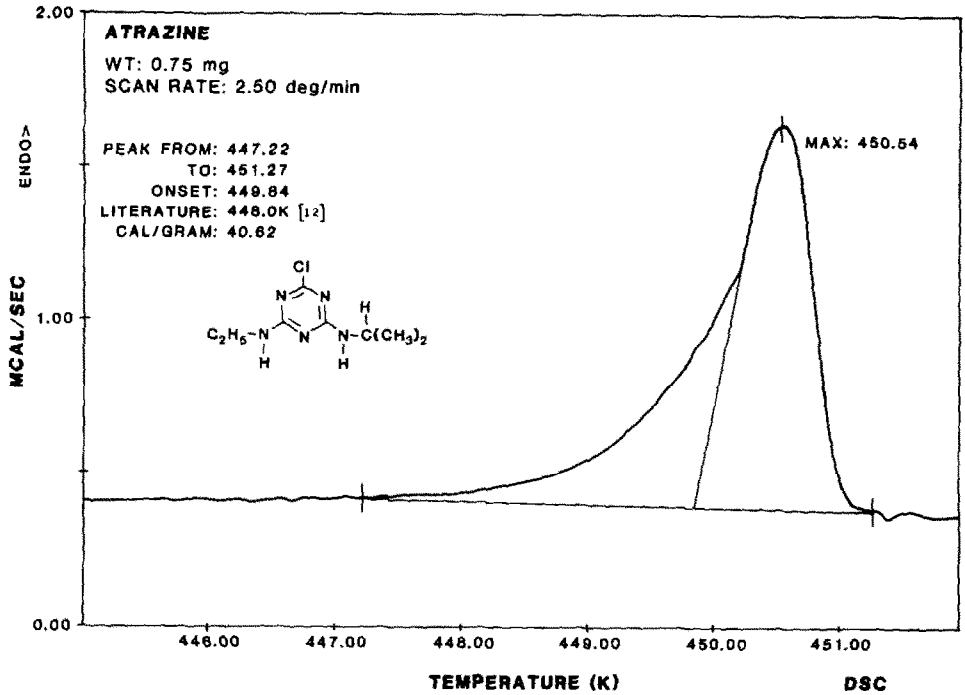

Fig. 8. DSC thermogram of atrazine.

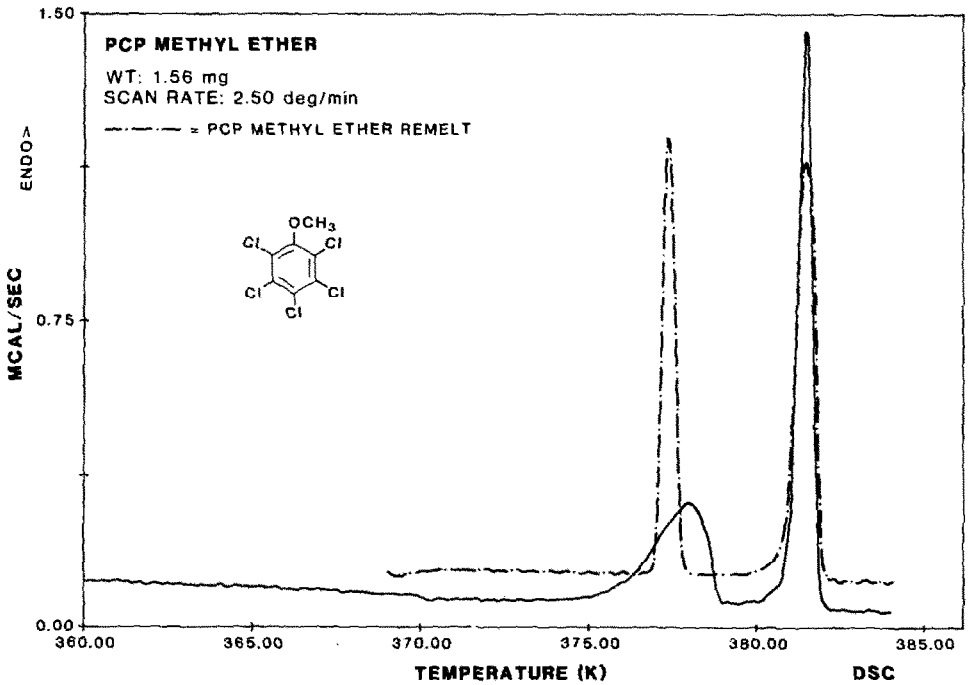

Fig. 9. DSC thermogram of PCP methyl ether.

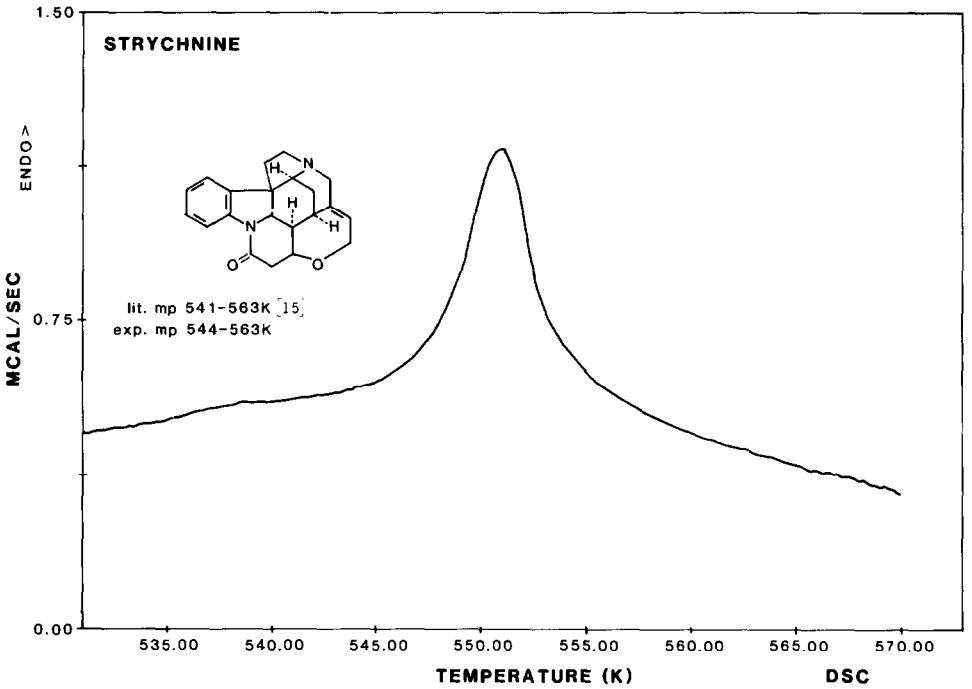

Fig. 10. DSC thermogram of strychnine.

butyric acid (MCPB), 2-methyl-4-chlorophenoxypropionic acid (MCPP), 2,4-D and 2,4,5-T acids. The pentachlorophenol (PCP)–methyl ether (pentachloroanisole) thermogram showed two distinct endotherms at 377 K and 381 K (Fig. 9). Remelting the sample caused the peaks to sharpen. Analysis of this compound by GC/MS indicated very high purity. The PCP–methyl ether sample may have retained a dimorphic form. This compound was not included in Table 1.

(8) Alkaloids

Many organic amines or alkaloids proved amenable to purity determination by DSC. However, strychnine produced a symmetrical peak with a convex baseline (Fig. 10), indicating m.p. 541–563 K (literature m.p. 544–563 K dependent on rate of heating). While this thermal behavior, lacking a normal endotherm and melting point, rendered our sample of strychnine not amenable to purity determination by DSC, a thermogram consistent with reported behavior was produced.

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