TECHNICAL NOTE

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A New Infrared Spectral Library of Controlled and Noncontrolled Drug Standards Using Internal Reflection Spectroscopy

REFERENCE: Koulis CV, Hymes KJ, Rawlins JL. A new infrared spectral library of controlled and noncontrolled drug standards using internal reflection spectroscopy. J Forensic Sci 2000; 45(4):876–881.

ABSTRACT: An infrared spectral library containing 455 controlled and noncontrolled solid drug standards was generated using internal reflection spectroscopy. All attenuated total reflection (ATR) spectra were obtained with small diamond internal reflection elements. ATR spectra will have minor variations from transmission spectra commonly found in commercial infrared libraries.

KEYWORDS: forensic science, infrared spectroscopy, attenuated total reflection, internal reflection spectroscopy, drug, substance abuse, library, controlled substance

An infrared spectral library was generated using internal reflection spectroscopy. Forensic drug analysis by internal reflection spectroscopy is a new application of an established infrared method. Attenuated total reflection spectra are produced when samples are placed in optical contact with the surface of an internal reflecting element. Internal reflection elements (IREs) must have a high refractive index and resist both mechanical damage and chemical attack when samples are pressed into contact with their surfaces. To best meet these requirements, internal reflection FT-IR accessories with small diamond IREs were selected to generate this spectral library.

Internal reflection spectroscopy has experienced increased application for infrared analysis, and ATR spectral libraries are needed for forensic drug analysis. ATR drug analysis is now being used with limited published ATR spectral data for comparison. The ATR spectra are similar to transmission spectra, but with some differences. The minor differences are a direct consequence of the transmission and reflection process. The ATR spectra of 455 controlled and noncontrolled standards were collected. These spectra are complied into an ATR spectral library for forensic drug analysis.

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Received 16 July 1999; and in revised form 5 Oct. 1999; accepted 11 Oct. 1999.

Procedure

All 455 solid standards were obtained from various sources including, but not limited to Sigma, Applied Science, K&K, USP, Brinkmann, Aldrich, and Mallinckrodt. The standards selected were obtained from the primary drug standards of the Illinois State Police Joliet Forensic Science Laboratory, Joliet, Illinois. Each standard is labeled with its originating source and lot number.

ATR spectra were obtained using a Mattson Genesis I Fourier Transform Infrared Spectrometer (FT-IR) with a Golden Gate™ single reflection diamond ATR accessory and sapphire anvil (Grasby Specac, Inc.), a Gateway 2000 computer equipped with the WinFIRST program, and a Hewlett Packard Laser Jet 5 printer. The following parameters were used: starting frequency of 4000 cm^{-1}, ending frequency of 500 cm^{-1}, 4 cm^{-1} digital resolution, 36 scans, a triangle apodization and a gain of 1. Background and blank spectra were collected every five samples. The spectra were also peak-picked using a threshold method with a cubic spline filter, a peak sensitivity of 1, and a peak column of 3.

A minimal amount of each solid standard was applied to the surface of the diamond. Preceding sample collection, the bridge was gently clamped and the sample clamp hand-tightened.

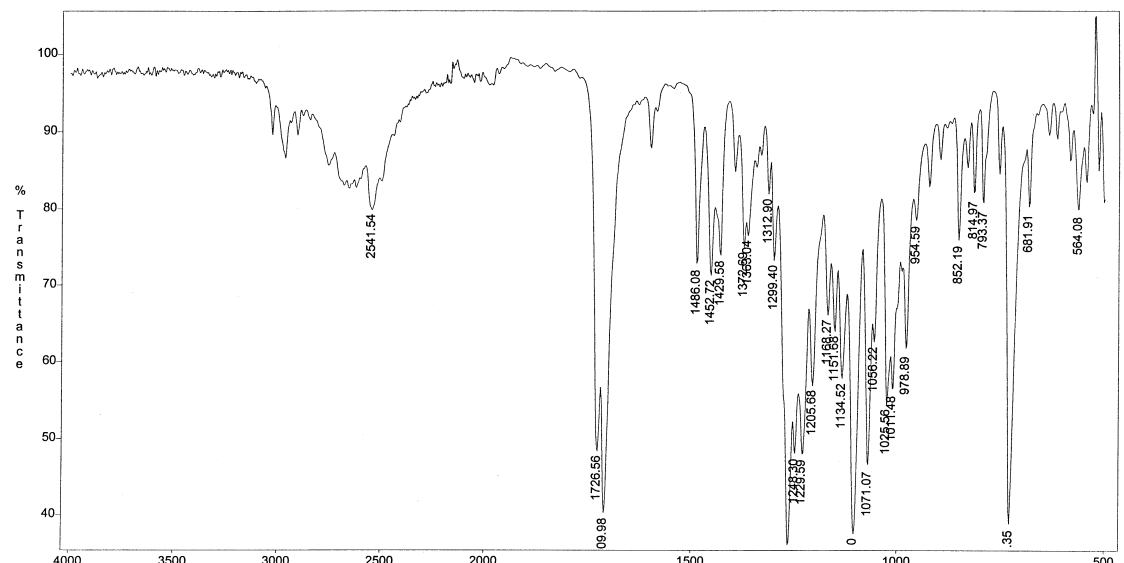
A macro was developed that would save the data to the a:\ drive. These data include the interferogram, the generated ATR spectra with report, and the generated peak-picked spectra with report. The macro prints a copy of each spectrum with report. The macro will also place the ATR spectra into a specified c:\ drive library within the WinFIRST program. The library specified was "goldgate." The macro can be seen in Fig. 1.

Results

Upon completion of sample collection, each spectrum was manually compared with various reference material (1–3) and in-house standard transmission spectra. This comparison was not to confirm the drug identity using transmission spectra, but to determine if unexpected peaks were omitted or added to the ATR spectra. If this inspection found the spectrum to be unacceptable, then this sample was reanalyzed using the same process. Of the 455 solid standards collected, 15 solid standards were labeled as unusable. These spectra remain in the library marked with an asterisk (*) at the beginning of the title information. Examples of commonly seen drugs can be found in Figs. 2*a* through 2*f*.

```
closeallwindows
E = "a:\"
bench:method_name= "gga.ini"
cd E
bench:scan
enter  A "Please enter sample file name"
save A
sample :info
plot "ppgg.ini"
cd E
pks:peakColumns = "three"
pks:peakFilter = "spline"
pks:peakMethod = "threshold"
pks:peakSensitivity = 1
pks:pick
enter C "Please enter report File name"
report:name = C
report:write
cd E
sample:show
enter D "Please enter annotated file name"
save D
plot "ppgg.ini"
add2lib "goldgate"
cd E
```

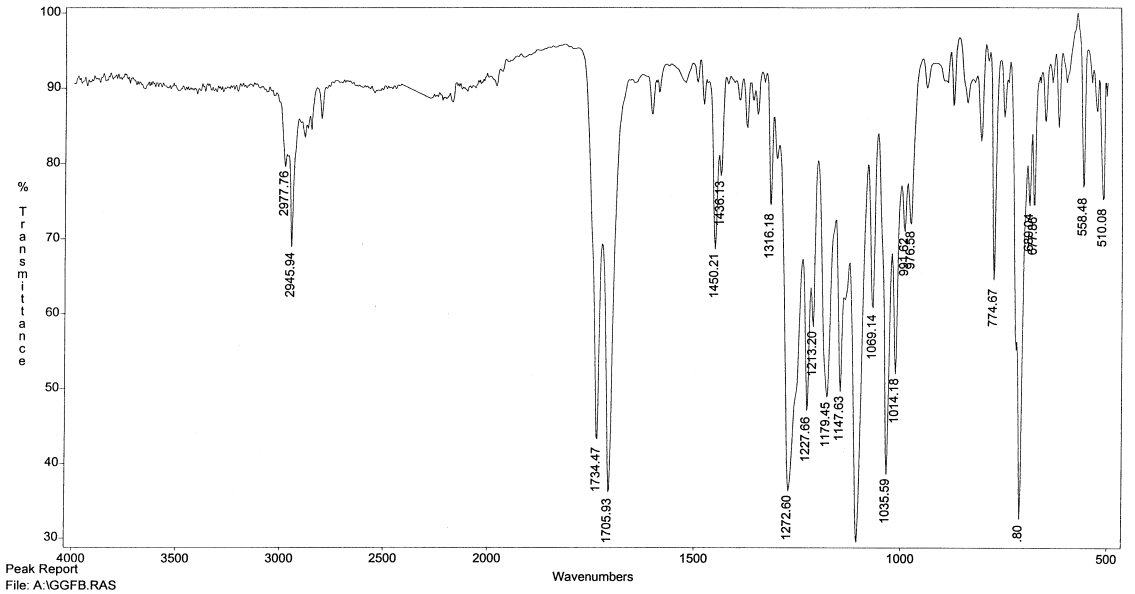
FIG. 1—*The macro ggadrive developed to obtain data.*



Peak Report
File: A:\GGHCL.RAS
Title: Cocaine HCl
Filter: Cubic Spline

cm-1	%T	cm-1	%T	cm-1	%T
564.08	79.67	681.91	79.98	729.35	38.72
793.37	80.42	814.97	81.72	852.19	75.83
954.59	78.43	978.89	61.39	1011.48	56.06
1025.56	54.33	1056.22	62.43	1071.07	46.23
1105.40	37.47	1134.52	57.70	1151.68	63.84
1168.27	66.00	1205.68	56.80	1229.59	47.75
1248.30	47.87	1264.50	35.92	1299.40	73.11
1312.90	81.82	1363.04	76.40	1372.69	74.81
1429.58	73.69	1452.72	71.16	1486.08	72.49
1709.98	40.11	1726.56	48.26	2541.54	79.81

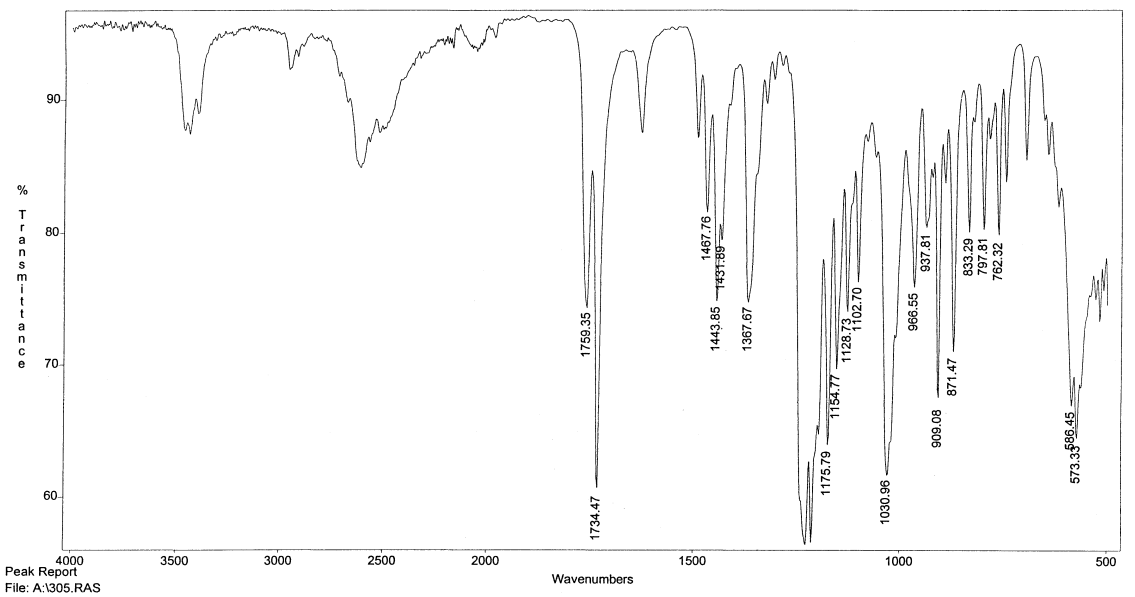
FIG. 2*a*—*A peak-picked spectra of cocaine hydrochloride.*



Peak Report
File: A:\GGFB.RAS
Title: Cocaine Base
Filter: Cubic Spline

cm-1	%T	cm-1	%T	cm-1	%T
510.08	74.82	558.48	76.25	677.86	73.73
689.04	74.19	711.80	32.58	774.67	64.13
976.58	71.80	991.62	70.90	1014.18	51.93
1035.59	38.56	1069.14	60.48	1107.52	29.37
1147.63	49.60	1179.45	48.75	1213.20	58.23
1227.66	46.79	1272.60	36.31	1316.18	73.92
1436.13	78.26	1450.21	68.63	1705.93	35.88
1734.47	42.73	2945.94	68.73	2977.76	79.59

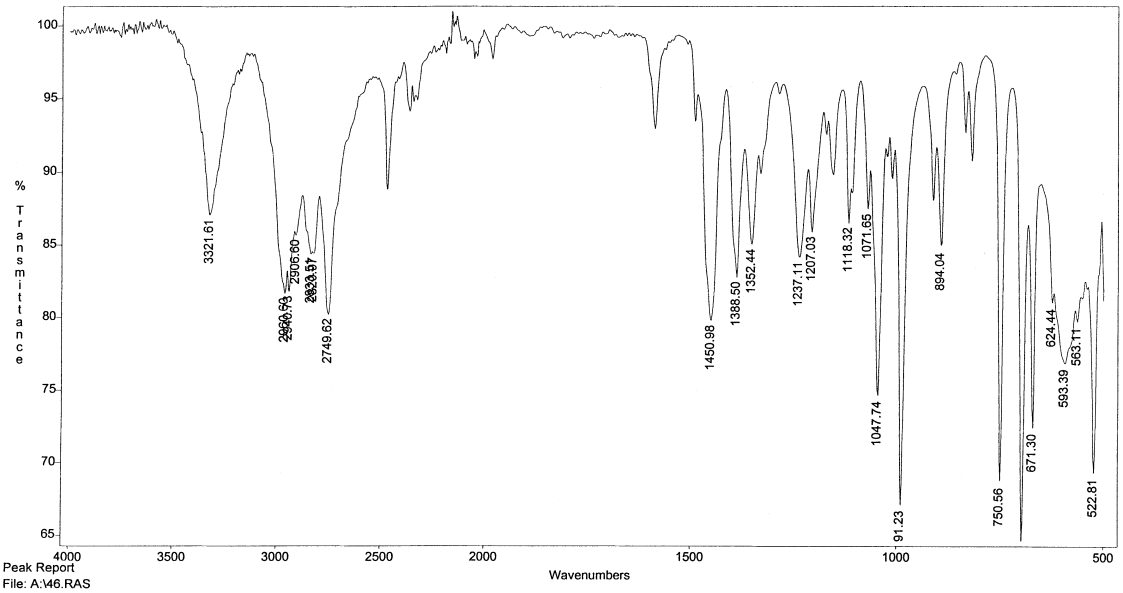
FIG. 2*b*—*A peak-picked spectra of cocaine base.*



Peak Report
File: A:\305.RAS
Title: Diacetylmorphine HCl (Heroin HCl) USP I-1 C-I
Filter: Cubic Spline

cm-1	%T	cm-1	%T	cm-1	%T
573.33	64.36	586.45	66.89	762.32	79.69
797.81	80.10	833.29	80.04	871.47	70.96
909.08	67.05	937.81	80.37	966.55	75.86
1030.96	61.60	1102.70	76.18	1128.73	73.83
1154.77	69.59	1175.79	63.79	1214.94	56.54
1229.01	56.32	1367.67	74.69	1431.89	79.32
1443.85	74.69	1467.76	81.57	1734.47	60.38
1759.35	74.24				

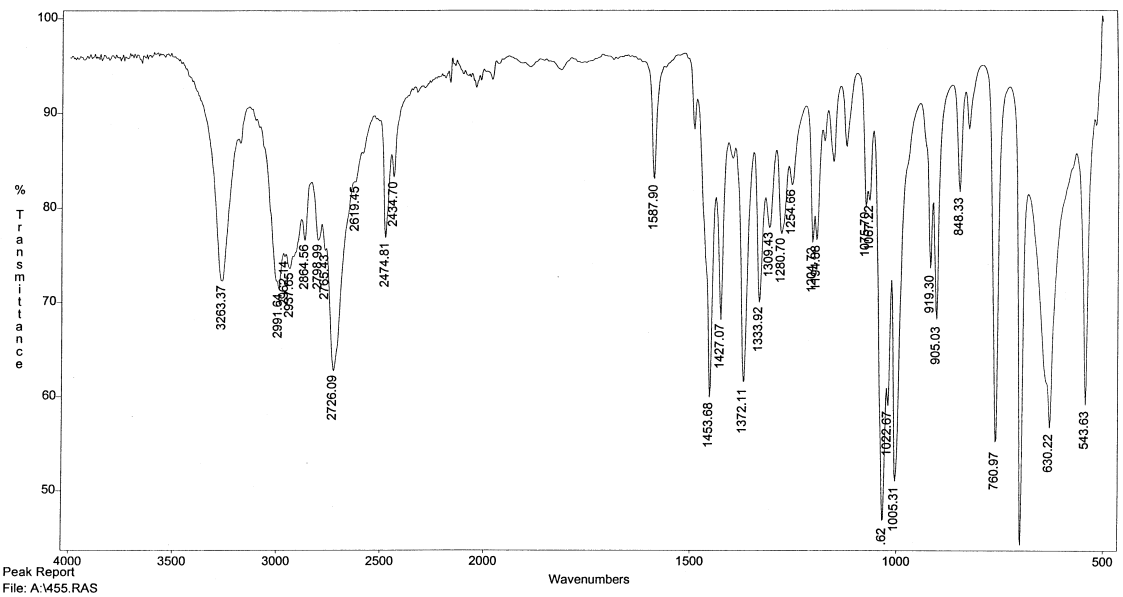
FIG. 2*c*—*A peak-picked spectra of heroin hydrochloride.*



Peak Report
File: A:\46.RAS
Title: Ephedrine HCl ICN 29833-A C-IV
Filter: Cubic Spline

cm-1	%T	cm-1	%T	cm-1	%T
522.81	69.29	563.11	79.69	593.39	76.82
624.44	80.99	671.30	72.38	697.53	64.48
750.56	68.66	894.04	84.86	991.23	67.10
1047.74	74.52	1071.65	87.41	1118.32	86.49
1207.03	85.88	1237.11	84.14	1352.44	85.02
1388.50	82.75	1450.98	79.74	2749.62	80.19
2820.97	84.43	2833.51	84.35	2906.60	85.67
2940.73	81.78	2960.60	81.65	3321.61	87.08

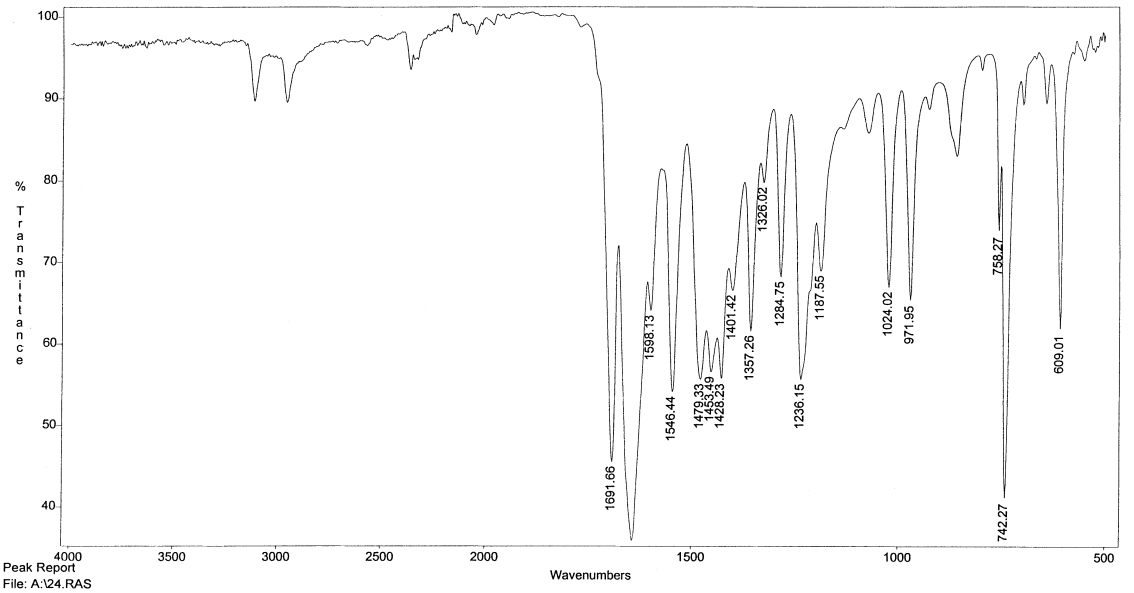
FIG. 2*d—A peak-picked spectra of ephedrine hydrochloride.*



Peak Report
File: A:\455.RAS
Title: Pseudoephedrine HCl (+-Ephedrine) Sigma 48C-0325 NS
Filter: Cubic Spline

cm-1	%T	cm-1	%T	cm-1	%T
543.63	59.06	630.22	56.61	700.80	43.54
760.97	54.75	848.33	81.71	905.03	68.00
919.30	73.47	1005.31	50.87	1022.67	58.88
1034.62	46.47	1067.22	80.68	1075.70	80.02
1194.88	76.47	1204.72	76.24	1254.66	82.39
1280.70	77.26	1309.43	77.88	1333.92	69.92
1372.11	61.28	1427.07	68.14	1453.68	59.77
1587.90	82.87	2434.70	83.21	2474.81	76.80
2619.45	82.74	2726.09	62.69	2765.43	75.49
2798.99	76.58	2864.56	76.55	2937.65	73.58
2962.14	74.83	2991.64	71.38	3263.37	72.25

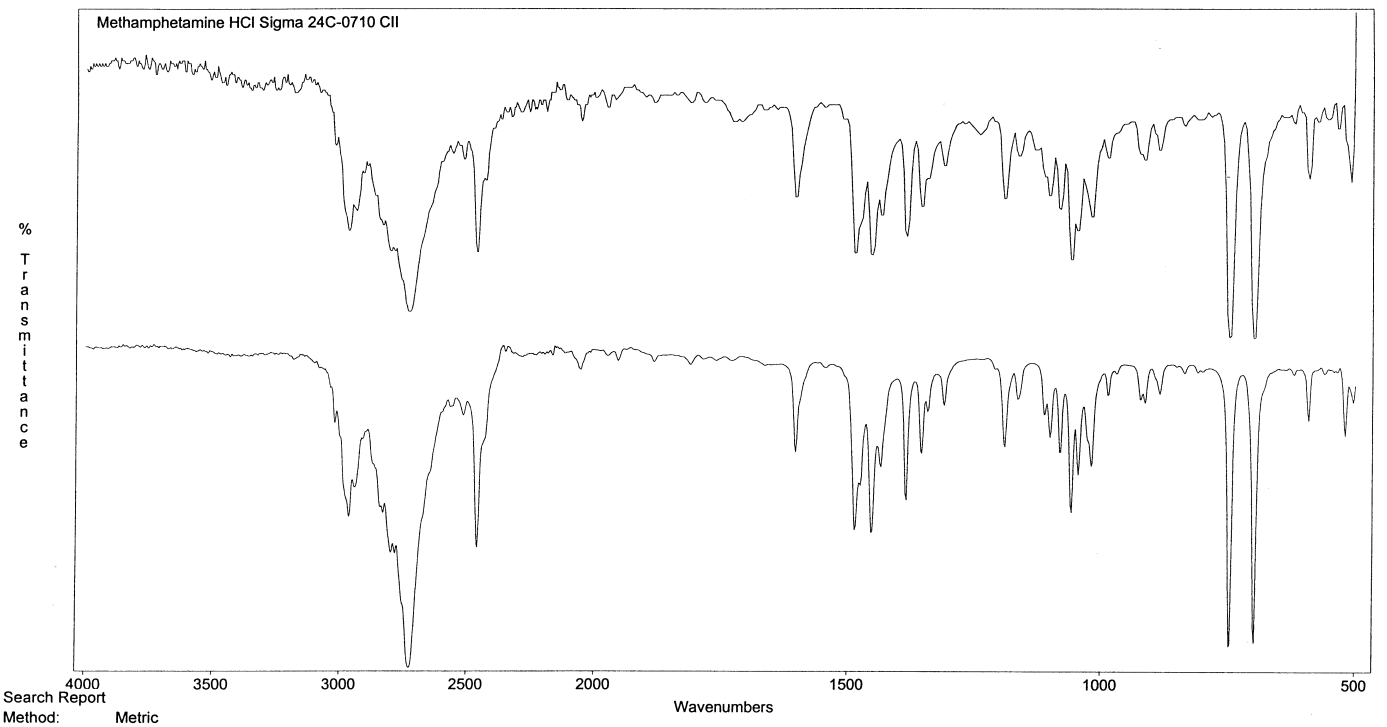
FIG. 2*e—A peak-picked spectra of pseudoephedrine hydrochloride.*



Peak Report
File: A:\24.RAS
Title: Caffeine Applied Science 204 NS
Filter: Cubic Spline

cm-1	%T	cm-1	%T	cm-1	%T
609.01	61.78	742.27	41.16	758.27	73.85
971.95	65.37	1024.02	66.92	1187.55	68.91
1236.15	55.63	1284.75	68.17	1326.02	79.76
1357.26	61.52	1401.42	66.50	1428.23	55.65
1453.49	56.51	1479.33	55.65	1546.44	54.10
1598.13	64.02	1642.67	35.81	1691.66	45.49

FIG. 2*f*—*A peak-picked spectra of caffeine.*

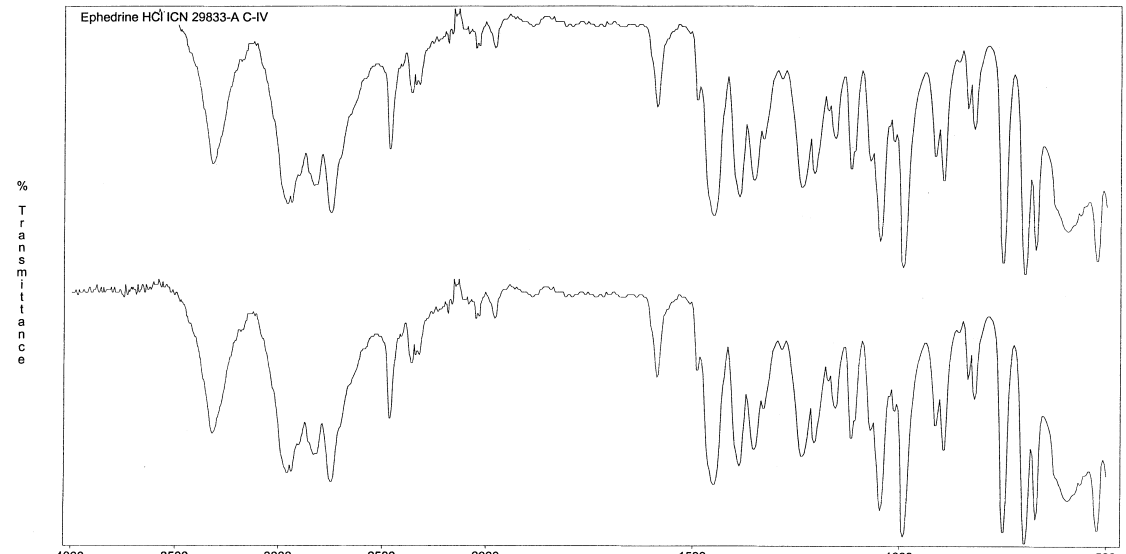


Search Report
Method: Metric
Algorithm: Correlation Coefficient
Libraries: goldgate
Regions: (Full Spectrum)

Results for CVK1.ras

1	goldgate	76	0.96	Methamphetamine HCl Sigma 24C-0710 CII
2	goldgate	299	0.83	Cyclopentamine HCl Lilly 2NK26 NS
3	goldgate	379	0.82	Propylamphetamine HCl Applied Science 1604 NS
4	goldgate	53	0.74	Fencamfamine HCl Aldrich HH061837 C-IV
5	goldgate	52	0.72	Fencamfamine HCl Aldrich HH 061837 C-IV
6	goldgate	170	0.72	Nortriptyline HCl Lilly 5BW06 NS
7	goldgate	194	0.70	Protriptyline HCl MSD L-590 NS
8	goldgate	370	0.65	PCP N-Ethyl Analog HCl Applied Science 2 C-I
9	goldgate	157	0.63	Methcathinone HCl ISP CI
10	goldgate	326	0.63	Phenmetrazine HCl USP F-1 CII

FIG. 3—*Methamphetamine hydrochloride library search results.*



Results for EPHSRCH.ras

1	goldgate	46	0.99	Ephedrine HCl ICN 29833-A C-IV
2	goldgate	98	0.76	Phenylpropanolamine HCl Sigma 90F-0404 NS
3	goldgate	445	0.71	Norcodeine HCl Trihydrate Alltech 120387 C-II
4	goldgate	371	0.71	*PCP-4-Hydroxy Metabolite HCl Applied Science 4 C-I
5	goldgate	328	0.71	Procyclidine HCl USP F NS
6	goldgate	258	0.69	Akineton HCl (Biperiden) Knoll 6724 NS
7	goldgate	376	0.69	Phenzocine HBr Applied Science 183 C-II
8	goldgate	455	0.69	Pseudoephedrine HCl (+-Ephedrine) Sigma 48C-0325 NS
9	goldgate	45	0.68	L-Ephedrine ICN 14324-A C-IV
10	goldgate	184	0.68	Phenyleprine HCl SKF 8228 NS
11	goldgate	407	0.67	Inosital NS
12	goldgate	181	0.66	Phenmetrazine Geigy SN49415 C-II
13	goldgate	49	0.65	Ephedrine Sulfate Brinkmann C-IV
14	goldgate	264	0.65	Amodiaquine P-D 230370 NS
15	goldgate	418	0.65	Pyridoxamine Dihydrochloride Sigma 94H0035
16	goldgate	231	0.65	Diphenidol HCl SKF GAC-3941 NS

FIG. 4—*Ephedrine hydrochloride library search results.*

When the library was complete, validation tests were performed using street samples and secondary laboratory standards. The library was found to be accurate in matching unknowns to the library and is currently being used in routine analysis (Figs. 3 and 4).

Conclusion

ATR is a confirmatory technique for analyzing controlled and noncontrolled substances in the forensic community. The small size of sample, ease of sample preparation, speed of analysis, and reproducibility of spectra make this an ideal method for drug analysis. Because there are differences between transmission and ATR spectra, exact matching of these spectra is impossible. The addition of this ATR spectral library gives the forensic scientist using ATR a new database to more quickly, accurately, and confidently analyze drugs.

Acknowledgments

Matt Aven and Jackie Bastyr from Mattson Instruments for their help with the macro, Arran Bibby and Dr. John A. Reffner from Sensir Technologies for their scientific support, and the Illinois State Police. Thank you.

References

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2. Mills T, Roberson JC. Instrumental data for drug analysis. 2nd ed. Vols. 1–4. New York, Amsterdam, London: Elsevier, 1987.
3. Mills T, Roberson JC, McCrudy H, Wall W. Instrumental data for drug identification. 2nd ed. Vol. 5. New York, Amsterdam, London: Elsevier, 1992.

Additional information and reprint requests:
A complete copy of the library is available to interested legitimate researchers and can be obtained through arrangements with the corresponding author.

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