



Designation: E 204 – 98 (Reapproved 2002)

Standard Practices for Identification of Material by Infrared Absorption Spectroscopy, Using the ASTM Coded Band and Chemical Classification Index¹

This standard is issued under the fixed designation E 204; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These practices describe a data system generated from 1955 through 1974. It is in world-wide use as the largest publicly available data base. It is recognized that it does not represent the optimum way to generate a new data base with the most modern computerized equipment.

1.2 These practices describe procedures for identification of individual chemical substances using infrared absorption spectroscopy and band indexes of spectral data. Use of absorption spectroscopy for qualitative analysis has been described by many (1-8),² but the rapid matching of the spectrogram of a sample with a spectral data in the literature by use of a band index system designed for machine sorting was contributed by Kuentzel (9). It is on Kuentzel's system that the ASTM indexes of absorption spectral data are based.

1.3 Use of these practices requires, in addition to a recording spectrometer and access to published reference spectra, the encoded data and suitable data handling equipment.³

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 168 Practices for General Techniques of Infrared Quantitative Analysis⁴

E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers⁴

E 1252 Practice for General Techniques for Qualitative Infrared Analysis⁴

3. Summary of Practices

3.1 A representative sample of the material to be analyzed is separated into its individual components, if required, and each component is introduced into a suitable sample cell or matrix, mainly according to its physical state. The spectrum is recorded over a characterizing range. The choice of spectral range and instrument is dictated by a general consideration of the chemical nature of the sample (3-5). A note is made of the spectral positions of prominent absorption bands and, optionally, of known chemical and physical properties of the material. The qualitative chemical composition of the material may then be identified by searching the coded data file for compounds having matching characteristics. Details on searching procedures are available elsewhere.⁵ Details of the code are in the following sections.

4. Apparatus

4.1 *Infrared Spectrophotometer*—A spectrophotometer with capabilities equivalent to an instrument with a rock salt prism operated under parameters compatible with Analytical Spectra (8, 10) and with wavelength accuracy to 0.05 μm by comparison with the indene spectrum in Practice E 932.

4.2 Laboratory procedures for obtaining spectra are described in Refs (3-5) and in Practices E 168, and E 1252.

4.3 *Data-Handling Equipment*—It is possible to convert data on the ASTM magnetic tape to IBM cards, and to use sorters or collators to manipulate the data. However, the file is large and it is more efficient, and with good software, more effective, to use computers. These may be either dedicated or time-shared. Thus, the minimum equipment requirement is a

¹ These practices are under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy and are the direct responsibility of Subcommittee E13.03 on Infrared Spectroscopy.

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² The boldface numbers in parentheses refer to the list of references at the end of these practices.

³ The *ASTM Infrared Spectral Index, AMD 33* and its supplements may be purchased in the form of magnetic tapes, from Sadtler Research Labs., Inc., 3316 Spring Garden St., Philadelphia, PA 19104.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

⁵ Publicly available systems are as follows: *IRGO*, Chemir Labs., 761 W. Kirkham, St. Louis, MO 63122; *SPiR* (Canada only), National Research Council, 100 Sussex Dr., Ottawa, Ontario, Canada K1A 0R6.

computer, a program, and the coded data (and either batch processing facilities) or a teletypewriter or terminal with modem for accessing these resources⁵ for interactive searches.

5. Index

5.1 The index data on approximately 145 000 spectra are available on magnetic tape. The main absorption bands of each spectrum are coded to the nearest 0.1 μm .

5.2 In addition to the code for spectral data of chemical substances, there are codes for chemical-structure classification, empirical formula, melting or boiling point, and serial number reference. Other codes include data on sample state, wavelength intervals of strongest bands, and no-data areas. For a given substance, the coded spectral data are almost invariably unique as is the pattern for coded chemical structure and physical properties. Variables may be searched in any desired combination to locate a standard spectrum similar to that of a sample of unknown composition, to correlate type of structure with absorption band positions, to locate spectra of compounds having given structural features in common, and in other ways that are too numerous to include here.

5.3 Spectral and chemical data from the user's own laboratory may be coded in a compatible system from details given in subsequent sections.

5.4 Molecular formula-name tabulations comprise complementary data systems for use in conjunction with the spectral band codes and chemical classification tapes. These carry the molecular formulas, chemical names, and reference serial numbers for the compounds included in the indexes described in 5.1 and 5.2. The tapes are commercially available and the indexes have been published in book form as alphabetical, numerical, and molecular formula indexes (11,12,13). These books enable one to determine the name of the compound involved from a knowledge of the serial number of a spectrogram or to locate a published standard spectrogram for a compound when the name is known. The serial-number listing permits one to obtain the names of possible solutions to analytical problems from spectra serial numbers produced by search operations even though complete files of standard spectra (as listed in Table 1) are not at hand. Often the name of the compound together with other available information will suffice; however, it is desirable to have as many standard spectra as feasible on hand for detailed study and comparison, because positive identification depends upon matching the unknown spectrum with one from published material or one obtained from a *bona fide* sample of the compound. The molecular formula and alphabetical indexes are useful for accessing band data for a suspected answer to an unknown.

6. General

6.1 The system described below is designed to handle the spectral absorption data obtained in the spectral range from 2 to 16 μm , and the system provides for a band-position coding resolution of 0.1 μm .

6.2 The original coding was on an IBM card format. The numerical values therefore correspond to columns and rows. See Fig. 1.

6.3 Columns 1 through 15 are used for coding absorption band positions.

TABLE 1 Catalogs of Spectrograms Covered by ASTM Punched Cards Indexing Infrared Absorption Data

A	API Research Project 44 ^A
B	User's own file of spectrograms ^B
C	Sadtler catalog of spectrograms ^C
D	NRC-NBS file of spectrograms ^D
E	Literature
F	Documentation of Molecular Spectroscopy ^F
G	Coblentz Society Spectrograms ^F
H	Chemical Manufacturer's Association (CMA) ^G
J	Infrared Data Committee of Japan ^H
K	Aldrich Library of Infrared Spectra ^I , 1970 Edition

^A American Petroleum Institute, Research Project 44, *Infrared and Ultraviolet Spectral Data*, Texas Agricultural and Mechanical College, College Station, TX, 1943 to date. Loose-leaf.

^B Users are encouraged to submit spectrograms (or the pure compound in some cases) to one of the other organizations listed. It is unlikely that any individual laboratory can code its spectral data and punch cards at the cost of the ASTM cards (about one cent each).

^C *Standard and Commercial Spectra*, Sadtler Research Laboratories, 3316 Spring Garden St., Philadelphia, Pa. 19104. Loose-leaf. The Sadtler organization also offers a "Spec-Finder" book method of matching spectrograms with those in its catalog.

^D *National Research Council-NBS Committee on Spectral Absorption Data*, National Bureau of Standards, Washington, D. C. 20025. Card file.

^E *The DMS System*, Butterworth Scientific Publications, London WC2. Distributed in U. S. by Butterworth, Inc., 7235 Wisconsin Ave., Washington, D. C. 20014.

^F *Coblentz Society Spectra*, sold by Sadtler Research Laboratories, 3316 Spring Garden St., Philadelphia, Pa. 19104 and The Coblentz Society, Inc., P.O. Box 9952, Kirkwood, MO 63122.

^G Chemical Manufacturer's Association (CMA) 1825 Connecticut Ave., N. W., Washington, D. C. Loose-leaf. Spectra are no longer available from CMA.

^H Infrared Data Committee of Japan, Sanyo Shuppan Doeki Co., Inc., Hoyu Bldg., 8, 2-chrome, Takaracho, Chuo-ku, Tokyo, Japan. Card file distributed in U. S. by Preston Technical Abstracts Co., 1718 Sherman Ave., Evanston, Ill.

^I The Aldrich Library of Infrared Spectra, Aldrich Chemical Co., 940 N. St. Paul St., Milwaukee, Wis. 53233.

6.4 The chemical classification code is in columns 32 through 57, and columns 58 through 62 provide for coding the number of C, N, O, and S atoms in the compound under consideration. A melting or boiling point is coded in 63 to 65. The rest of the card provides space for the private use of individual laboratories and the identification of the source of the coded data. The codes concerned with each of these areas are discussed separately.

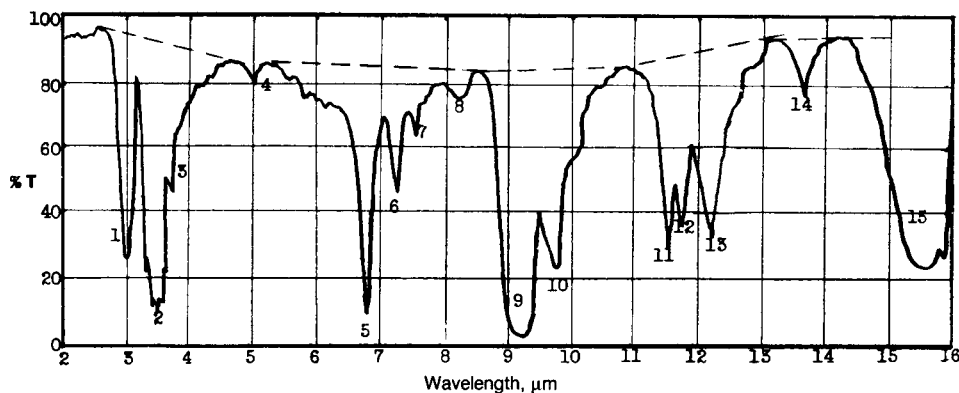
CODING OF INFRARED ABSORPTION BANDS (COLUMNS 1 THROUGH 25)

7. Codes for Absorption Band Positions

7.1 *Columns 1 to 15 of "A" Cards* (Note)—Coding is done in terms of wavelength in micrometres. From columns 1 through 15, the column number is taken as the whole number value of the absorption band, and the fractional part is rounded to the nearest 0.1 μm (values ending in five hundredths are considered as next higher tenths) and the number corresponding to the 0.1 μm value is added to the number of the column. Thus a band at 7.38 μm is coded to correspond to position 4 in column 7, for a value of 7.4. The coding resolution of 0.1 μm has been found to be adequate for searching and correlating published spectra.

NOTE 1—"A" is the designation for rock salt region infrared data (see 18.4).

7.2 *Columns 1 to 25 of "G" for Far-Infrared*—The coding of far-infrared absorption bands is done in terms of wavelength in micrometres. The whole number value of the band position



NOTE 1—The above hypothetical spectrogram is included to assist in describing the application of rules prescribing which bands to code and which to omit from the index card. It will be noted that band No. 9 is the strongest and has a transmittance value between 1 and 5 %; therefore all bands having a transmittance of 70 % or less as measured against a reasonably adjacent background should be coded. The dotted lines indicate what is meant by such an adjacent background. The distance by which coded bands must project from such a background is equal to one and a half units of the vertical scale. Applying this rule, one can code without question the following bands: No. 1, 2, 5, 6, 9, 10, 11, 12, 13, and 15, and furthermore, bands 2, 9 and 15 should receive the “y” overpunch code also. Band No. 5, while rather strong, is not expected to persist in considerably diluted samples of this material.

It will be noted that band No. 3 was not included. This is a case of a rather weak band on the side of a strong one which has no value in sorting and need not clutter up the card. Therefore it was omitted. On the other hand, band No. 10 was included as it is prominent enough to be used in sorting operations. Also, No. 12, which does not fit the coding criteria when measured from its immediately adjacent background, is included in those bands coded because it obviously is one of three rather strong bands which are close enough together to overlap appreciably. An ill-defined shoulder on the side of band No. 10 is ignored as is the fine structure in the No. 2 band. Band No. 14 represents a possible borderline case that should not be coded. A good rule is “when in doubt, leave it out.” The spectrogram is typical of many that appear published in the literature and serves to illustrate why a coding resolution of 0.1 μm is entirely adequate.

FIG. 2 Example of Infrared Curve

was coded the position was 13.5, or number 5 in column 13. In an unknown spectrogram, this same band might be read as 13.44, or if a longer cell path was used the band may have spread to the extent that one cannot be certain whether the minimum is 13.4 or 13.5 μm. In such a case, the search program should accept 13.4 or 13.5 μm, or both, and thus not miss the desired compound.

10. Negative Searching for the Analysis of Mixtures


10.1 When the unknown infrared spectrogram represents a mixture of two or more compounds in appreciable amounts, positive searching on the absorption band positions must

follow a procedure that considers the many possible combinations of bands that may characterize an individual constituent, since it is not known which bands are produced by each component. Such an approach may be carried out directly on the spectrogram of a mixture. However, considerable time may be saved if the bands are subjected to “negative” searching to eliminate all of the spectra that do have bands in regions of the spectrum where the unknown spectrogram does not have bands, since none of these could possibly be a component of the mixture. Positive searching of the reduced spectral file which results from the negative searching is more selective than searching the total file.

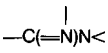
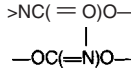
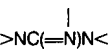
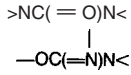
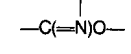
TABLE 2 Chemical Classification Code Chart Part A

Row	Column 32 Elements	Column 34 Structure	Row	Column 36 Code Units	Column 38 Miscellaneous	Row
0	O	acyclic	0	12 or more	solid	0
1	N	alicyclic	1	1	liquid	1
2	S	aromatic	2	2	gas	2
3	F	heterocyclic	3	3	organo-metallic	3
4	Cl	fused alicyclic	4	4	isotopic	4
5	Br, I	fused aromatic	5	5	indeterminate	5
6	P, Bi	fused heterocyclic	6	6	solution	6
7	As, Sb		7	7	polymer	7
8	Si, Ge	3 or 4-member ring	8	8	chelate	8
9	Sn, Pb	5-member ring	9	9	hydrate	9
X	B, Al	6-member ring	X	10	salt plate	X
Y	other	7-or more member ring	Y	11		Y

Row	Column 33 Unsaturation	Column 35 Rings—Chains	Row	Column 37 Substitutions	Column 39 Miscellaneous	Row
0	ring	rings	0	[mono]	cis	0
1	1	1	1	1 [1, 2]	trans	1

Row	Column 33 Unsaturation	Column 35 Rings—Chains	Row	Column 37 Substitutions	Column 39 Miscellaneous	Row
2	2	2	2	2 [1, 3]	spiro	2
3	3	3	3	3 [1, 4]	dextrorotary	3
4	4	4	4	4 [1, 2, 3]	levorotary	4
5	5	5	5	5 [1, 2, 4]	symmetrical	5
6	6	6	6	6 [1, 3, 5]	unsymmetrical	6
7	7	7	7	7 [1, 2, 3, 4]	vicinal	7
8	8	8	8	8 [1, 2, 4, 5]	salt	8
9	9	9	9	9 [1, 2, 3, 5]	inorganic ester	9
X		10	X	10 [penta]		X
						
Y	—C≡C—	11 or more	Y	[hexa]	inorganic	Y

Part B

Row	Column 40 C—H	Column 42 O	Column 44 N	Row	Column 46 S	Column 48 N—O	Row
0	—CH ₃ methyl	—C(=O)OH		0	—C(=S)S—		0
1	—C ₂ H ₅ ethyl	—C(=O)O—		1	—C(=S)H		1
2	—C ₃ H ₇ n-propyl	—C(=O)H	—CN	2	>C = S		2
3	—C ₃ H ₇ isopropyl	>C = O	—NC	3	—SC(=S)S—	—NCO	3
4	—C ₄ H ₉ n-butyl	—OC(=O)O—	—NH ₂	4	—SH	—OCN	4
5	—C ₄ H ₉ isobutyl	C(OR) ₄	>NH	5	—S—	>NNO ₂	5
6	—C ₄ H ₉ sec-butyl	—C(OR) ₃	>N—	6	—SS—	>NNO	6
7	—C ₄ H ₉ tert-butyl	—OH	>C = N—	7	>S ⁺	—NN(=O)—	7
8	—C ₅ H ₁₁ n-pentyl	—O—	= NN =	8	= S = S	—ONO ₂	8
9	—C ₆ H ₅ phenyl	—OO—	>NN<	9		—ON = O	9
X		other	= N≡N	X	other	other	X
Y		heterocyclic	other	Y	heterocyclic	heterocyclic	Y

Row	Column 41 C—H	Column 43 O	Column 45 N	Row	Column 47 S	Column 49 N—O	Row
0	—CH = CH ₂ vinyl	>O ⁺	—N = N—N<	0		—NO ₂	0
1	>C = CH ₂ methylene	—O ₃ —	—N=N ⁺	1		—NO	1
2	= CHCH ₃ ethylidene	>C(—O—) ₂	>N ⁺	2		= NO—	2
3	—CH ₂ CH = CH ₂ allyl		—NH ₄	3		> NO—	3
4	—CH = CHCH ₃ propenyl		>NCN	4		>N = O	3
5	—C(CH ₃) = CH ₂ isopropenyl		—N ₃	5			4
6	= C(CH ₃) ₂ isopropylidene			6			5
7	—C=CH ethynyl			7			6
8	—C=CCH ₃ 1-propynyl			8			7
9	—CH ₂ C=CH 2-propynyl			9			8
X	conjugated	conjugated	conjugated	X	conjugated	conjugated	9
Y				Y			X

Row	Column 50 N—	Column 52 O—S	Row	Column 54 N—O—S	Column 56 Elements	Row
0	>NC(=S)N<	—OC(=S)S—	0	>NC(=S)O—	Se, Te, Po	0
	—SC(=N)N<	—SC(=O)S—		>NC(=O)S—		
1	>NC(=S)S—	—OC(=S)O—	1	—C(=O)NS—	Ga, In, Tl	1
	—SC(=N)S—	—OC(=O)S—		—C(=S)NO—		
2	—C(=S)N<	—C(=S)O—	2	—OC(=N)S—	Zn, Cd, Hg	2
	—C(=N)S—	—C(=O)S—				
3		—S(O ₂)O—	3	—S(=O)N<	Cu, Ag, Au	3
4	—SCN	—S(=O)O—	4	>NS(O ₂)N<	Fe, Co, Ni, Mn	4
5	—NCS	—S(=O)S—	5	>NS(O ₂)O—	Cr, Mo, W, U	5
		—S(=S)O—				
6	>NSN<	S _x O ₆ (x = 2–6)	6	>NS(O ₂)—	V, Cb, Ta, Pa	6
7	= NS—	>SO ₂	7	>NS(=O)O—	Ti, Zr, Hf, Th	7
	> NS—					
8	—N = S	>S = O	8	—NSO	Se, Y, La, Ac	8

9	>S = N—	—OSO—	9		Ru, Rh, Pd, Os, Ir, Pt	9
X	other	other	X	other	rare earths	X
Y	heterocyclic	heterocyclic	Y	heterocyclic	heterocyclic	Y

Row	Column 51 N—S	Column 53 O—S	Row	Column 55 N—O—S	Column 57 Elements	Row
0		—OS(O ₂)O—	0		Li	0
1		—OS(=O)O—	1		Na	1
2			2		K	2
3			3		Rb, Cs	3
4			4		Be	4
5			5		Mg	5
6			6		Ca	6
7			7		Sr, Ba	7
8			8			8
9			9			9
X	conjugated	conjugated	X	conjugated	conjugated	X
Y			Y		other	Y

ORGANIC CHEMICAL CLASSIFICATION CODE (COLUMNS 32 THROUGH 57)

11. General

11.1 The chemical classification code for organic compounds is designed to present the chemical structure of such compounds in a convenient form for use in the preparation and use of ASTM indexes of absorption spectral data. The accompanying chart (Table 2) relates the code positions on the card in terms of column and row numbers to the coded items of structural features used to characterize compounds. Reference to codes are made by giving the column number followed by the row designations. For example, 32-0,2,y indicates positions 0,2, and “y” in column 32. The overpunch positions are referred to as “x” and “y” to avoid digital confusion, but they correspond to the 11 and 12 positions. While every effort was made to keep the codes simple and unambiguous, the complexity of some structures that must be coded requires that a few rules be provided in the interest of uniformity. These rules, together with notes on the interpretation of them, follow in a column-by-column discussion of the chart. At the end will be found general instructions for the application of the codes together with a number of examples (Table 3).

11.2 *Part A*—This section of the chart is concerned with providing a means of coding elements commonly found in organic materials; the number, size, and kind of gross structural features; the number and locations of code units or substituent groups of atoms upon these gross features; and a number of general descriptive terms that may be applied to the materials encountered.

11.2.1 *Column 32*—This column provides for the coding of the identity of elements commonly found in organic compounds. Carbon and hydrogen are not coded directly, but hydrocarbons are indicated when there are no value 32 codes. The code is the designated value for each different element regardless of the number of such elements in the compound. The coding of less common elements is provided for in columns 56 and 57. Whenever any of these elements or any not listed in the chart are coded, a code of “y” or “other” should be made in column 32.

11.2.2 *Column 33*—This column codes the type and location of unsaturated carbon-to-carbon bonds. In every case,

except for aromatic unsaturation, the presence of such unsaturation is coded as to type (that is, double bond or triple bond, or both), by 33-x or 33-y, or both. Numbers in this column are used to indicate the location of these unsaturated bonds subject to the following rules:

11.2.2.1 If the unsaturation is located in a ring, then a code of 33-0 is required. When this is lacking, it is understood that unsaturation in a chain is being coded.

11.2.2.2 Unsaturation at positions requiring numbers higher than nine, Greek letters, or primed numbers are not coded.

11.2.2.3 The use of the position codes is restricted to compounds containing a single chain, a single ring, or a fused ring system where the Geneva System for chains and the Patterson Ring Index for cyclic compounds can be applied without ambiguity.

11.2.2.4 Unsaturation in benzene rings, fused or otherwise, or in alicyclic rings as a result of fusion with aromatic rings is not coded here.

11.2.2.5 Where both cyclic and chain systems are present in a single compound and unsaturation is present in only one or the other, it is to be coded as to location.

11.2.2.6 Where both cyclic and chain systems are present in a single compound and both contain unsaturation, the position code is applied to the largest ring or fused ring system.

NOTE 2—Space for coding unsaturated hydrocarbon groups and conjugated unsaturation is provided for in column 41.

11.2.3 *Column 34*—This column is used to code the major structural features of a compound and is largely concerned with the type and size of rings. The use of these codes in describing a molecular structure is governed by the following rules:

11.2.3.1 An “acyclic” code is used whenever there are one or more carbon atoms which are not part of a ring. Thus, methane, benzaldehyde, toluene, ethyl benzene, and benzoic acid require “acyclic” codes, but phenol, aniline, and phenyl hydrazine would not.

11.2.3.2 Each individual type of ring present in a single molecule is coded by a single code. Each member of a fused system is coded separately if different types are involved. All rings other than aromatic or heterocyclic are considered alicyclic and only benzene rings are coded “aromatic.”