NBSIR 75-759

# Standard Reference Materials and Data For Raman Spectroscopy, Electron Paramagnetic Resonance, and Magnetic Moment Measurements

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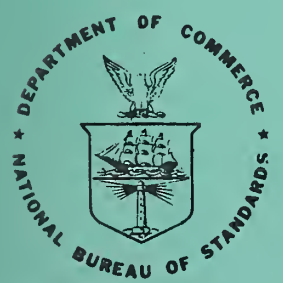


U S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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**U.S. DEPARTMENT OF COMMERCE, Rogers C.B. Morton, *Secretary***
**James A. Baker, III, *Under Secretary***
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**NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Acting Director***

# STANDARD REFERENCE MATERIALS AND DATA FOR RAMAN SPECTROSCOPY, ELECTRON PARAMAGNETIC RESONANCE, AND MAGNETIC MOMENT MEASUREMENTS


## ABSTRACT

This publication contains the analyses of three survey-questionnaires to assess the needs and markets for standards in Raman spectroscopy, electron paramagnetic resonance, and magnetic moment measurements. These analyses give the requirements and suggest the strategies to be followed for making each of the above three measurement methods more quantitative than they are at present. Some of the requirements are data cataloging, standards for data presentation, standard reference materials, and standard reference data.



Keywords: Electron paramagnetic resonance; magnetic moment; Raman spectroscopy; standard reference data; standard reference materials.

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# 1.0 INTRODUCTION

The Solid State Materials Section at the National Bureau of Standards conducts research on solid state materials with emphasis on their technologically important behavior which results from their optical, electrical, and magnetic properties. It interprets the mechanisms for such properties in terms of physical, structural, and chemical factors and develops measurement methods, data, and standards required to support selected technologies.

To continue our efforts on the provision of standard reference materials and data, we have used three survey-questionnaires to assess the needs and markets for standards in Raman spectroscopy, electron paramagnetic resonance (EPR), and magnetic moment measurements. In addition, we have used these surveys to determine the requirements for making such measurements more quantitative than they are at present. The detailed analyses of these three surveys are given, respectively, in parts 3.0, 4.0, and 5.0 of this publication.

Our general approach for these three surveys was to obtain mailing lists of workers who had a reasonable probability of using one or more of the above three measurement techniques. After the mailings were completed, we analyzed those questionnaires which were voluntarily returned to us. Because of limitations on the resources available to us, we did not seek responses from those who had not returned the questionnaires. Hence, our analyses were based upon volunteer responders and as such represented a lower bound on the size and needs of the potential beneficiaries of our standards services.

# 2.0 SUMMARY OF FINDINGS AND HIGHLIGHTS

We mention briefly in the next several paragraphs some highlights from these three surveys.

## 2.1 RAMAN SPECTROSCOPY

The magnitude of the response was 111 out of 285, or 39%. Some of our findings are listed below:

(1) Many respondents encounter problems because the Raman frequency shifts, relative band intensities, and depolarization ratios are not reported accurately.

(2) A definite interest in data compiling efforts exists among the respondents.

(3) Raman standard reference materials elicit strong, positive comments. Our analysis reveals two problems: namely, how do we measure the standard spectrum of a standard reference material? and, how do we transfer the necessary measurement technology to the user of the SRM? Standard reference materials will make Raman spectroscopy a more quantitative measurement science than it is at present.

(4) The setting of standards for data presentation is essential for the success of any SRM effort.

This survey is a first step for the National Bureau of Standards in its efforts to help promote standardization in the important measurement science of Raman spectroscopy.

Please direct inquiries on standards in Raman spectroscopy to Gregory J. Rosasco (telephone: 301-921-2780).

2.2 ELECTRON PARAMAGNETIC RESONANCE

Our EPR survey assesses the need for a standard reference material (SRM) by which to improve intensity measurements in electron paramagnetic resonance (EPR). As in Raman spectroscopy, such an EPR SRM will make EPR a more quantitative technique. The number of answered questionnaires is 175 out of 503 or 35%.

From our analysis, about one quarter of the EPR users is in physics, one quarter is in biomedicine, and the remaining half is in chemistry. By references to journals in which researchers in physics and in biomedicine publish we discern a trend for the number of EPR users in physics to decrease and the number of EPR users in biomedicine to increase. We cite here highlights of the survey:

(1) The EPR respondents need and want an intensity EPR SRM (93% say yes). Everyone who has attempted quantitative EPR measurements stated that the lack of standards presents great handicaps and difficulties.

(2) A standard reference material which results in EPR line intensity measurements accurate and precise to within 10% will satisfy the present needs of over half of the respondents.

(3) The purchasers of EPR SRM's will require technical help and advice, and particularly, detailed and extensive instructions on how to use the EPR SRM's; i.e., a challenge exists to transfer our technology in EPR to the EPR user community.

Please direct inquiries on standards for electron paramagnetic resonance to Te-Tse Chang (telephone: 301-921-2820).

2.3 MAGNETIC MOMENT MEASUREMENTS

The number of answered questionnaires is 297 out of 781 or 38%. The magnetic moment survey reveals that 87% of the 124 workers who returned questionnaires, and who stated that they need a magnetic moment SRM, already use some type of reference materials. Nickel is the most frequently used calibrant by this subset of workers. None of the workers who used a reference material state the accuracy of their own calibrant.

The value of the saturation magnetization for nickel given in the literature varies by 8% among reliable sources. Workers do not know which value is the correct one to use.

And finally, this survey shows that if NBS were to issue a magnetic moment SRM, then it should have the following properties:

(a) an accuracy within ± 1%,
(b) more than one size (perhaps a 1-mm and a 3-mm sphere),
(c) nickel will most likely be one of the calibrants,
(d) the price should be less than $150.00.

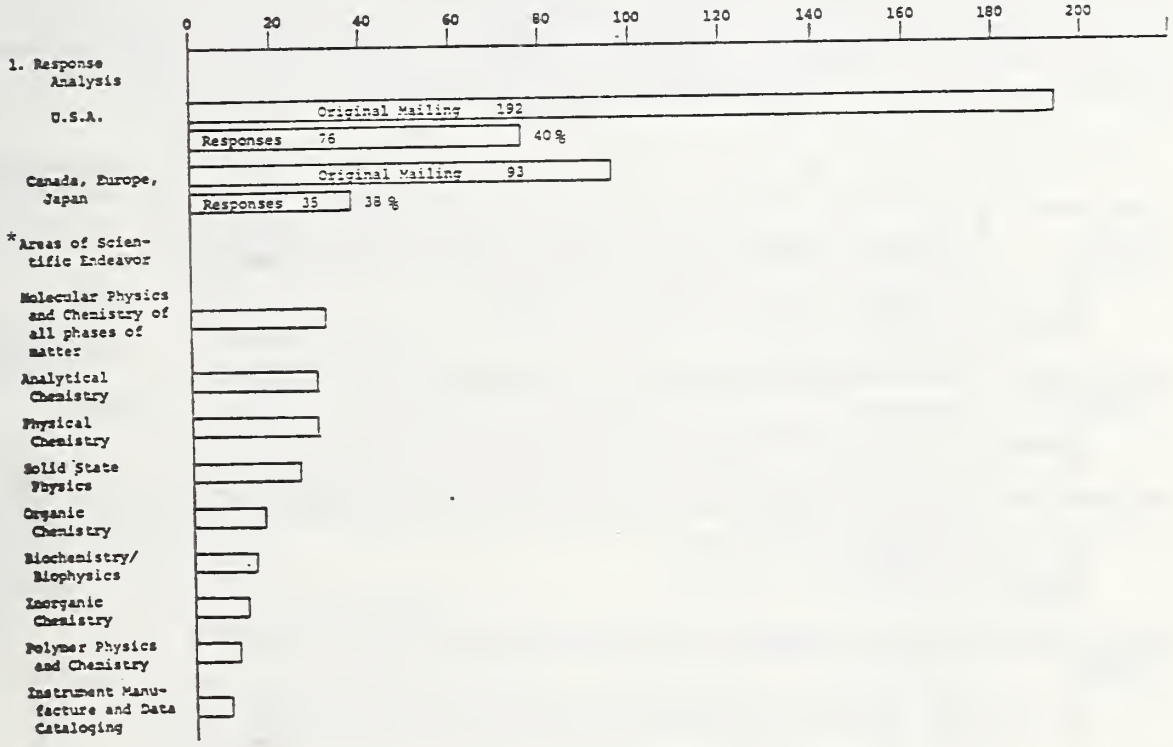
Please direct inquiries on standards for magnetic moment measurements to George A. Candela (telephone: 301-921-2780).

# 3.0 SURVEY REPORT ON STANDARDS FOR RAMAN SPECTROSCOPY

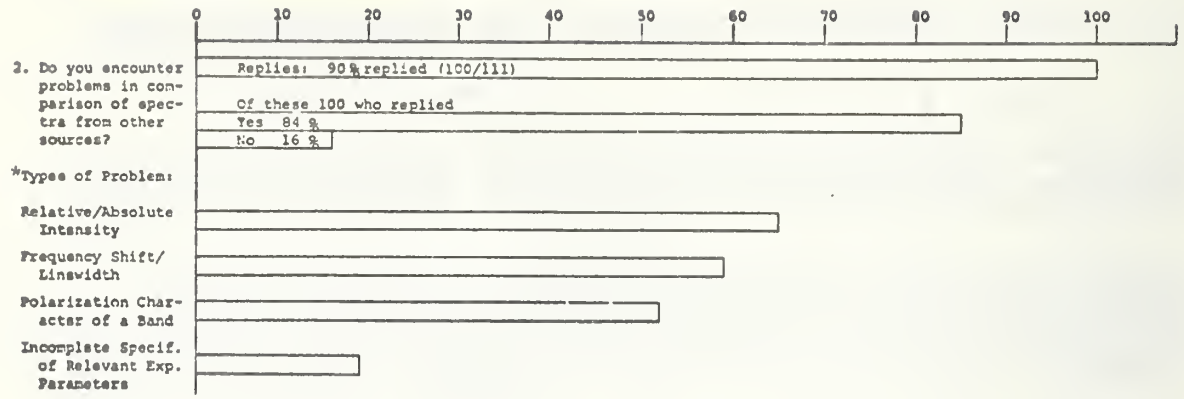
## 3.1 SUMMARY

The survey "Standards for Raman Spectroscopy" was distributed in January 1973. The numerical results, the analysis of these results, and conclusions derived from the survey are presented here.

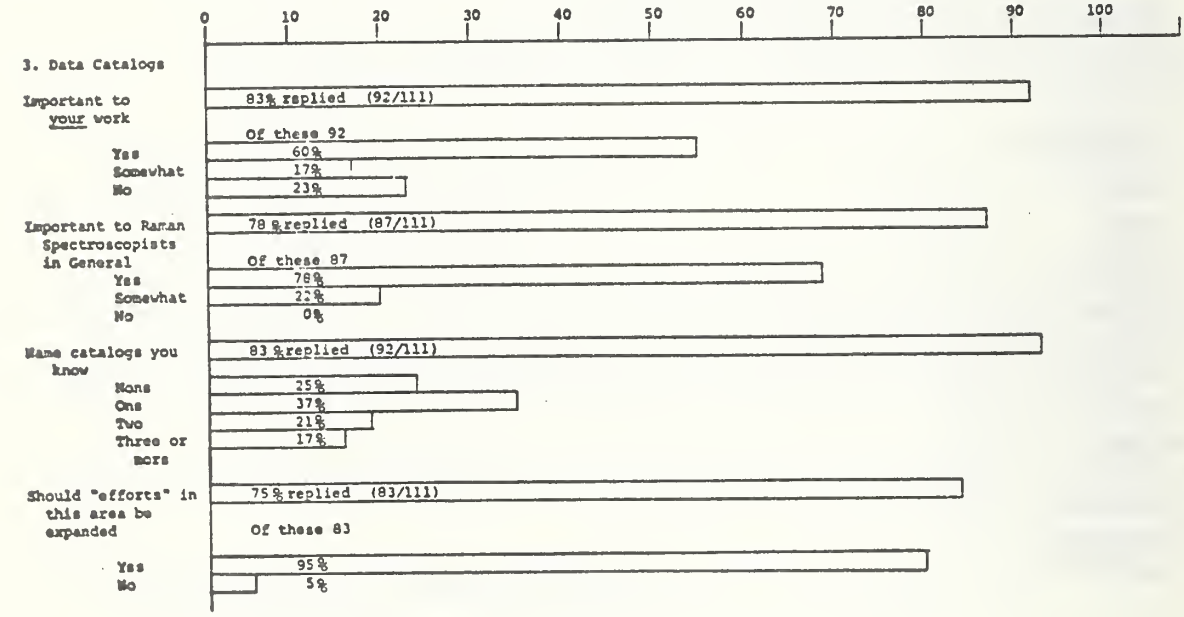
To summarize the results, the five major subject areas are presented in a graphical format below. Each subject area is briefly described in a paragraph following the graph. In the graphs, the number of respondents or the number of responses of a given type are plotted by the horizontal bars. Percentages (indicated by %) of relevant response totals are often provided; however, only numbers of respondents or responses are plotted. Categories in which a single respondent could give more than one reply are indicated by an asterisk (*).



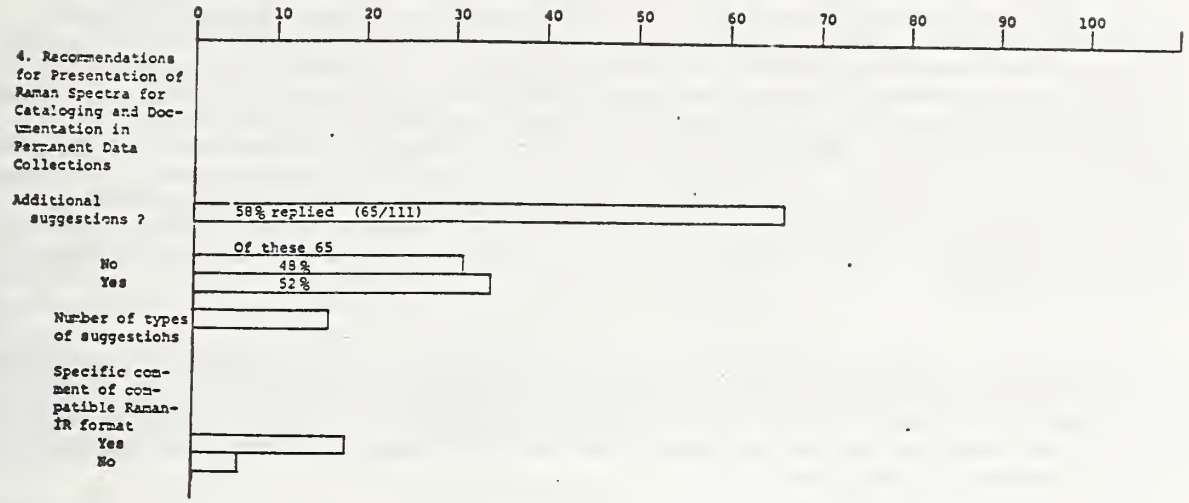

The magnitude of the response is 39%. The breakdown of the areas of scientific endeavour is based on the descriptive titles most used by the respondents.



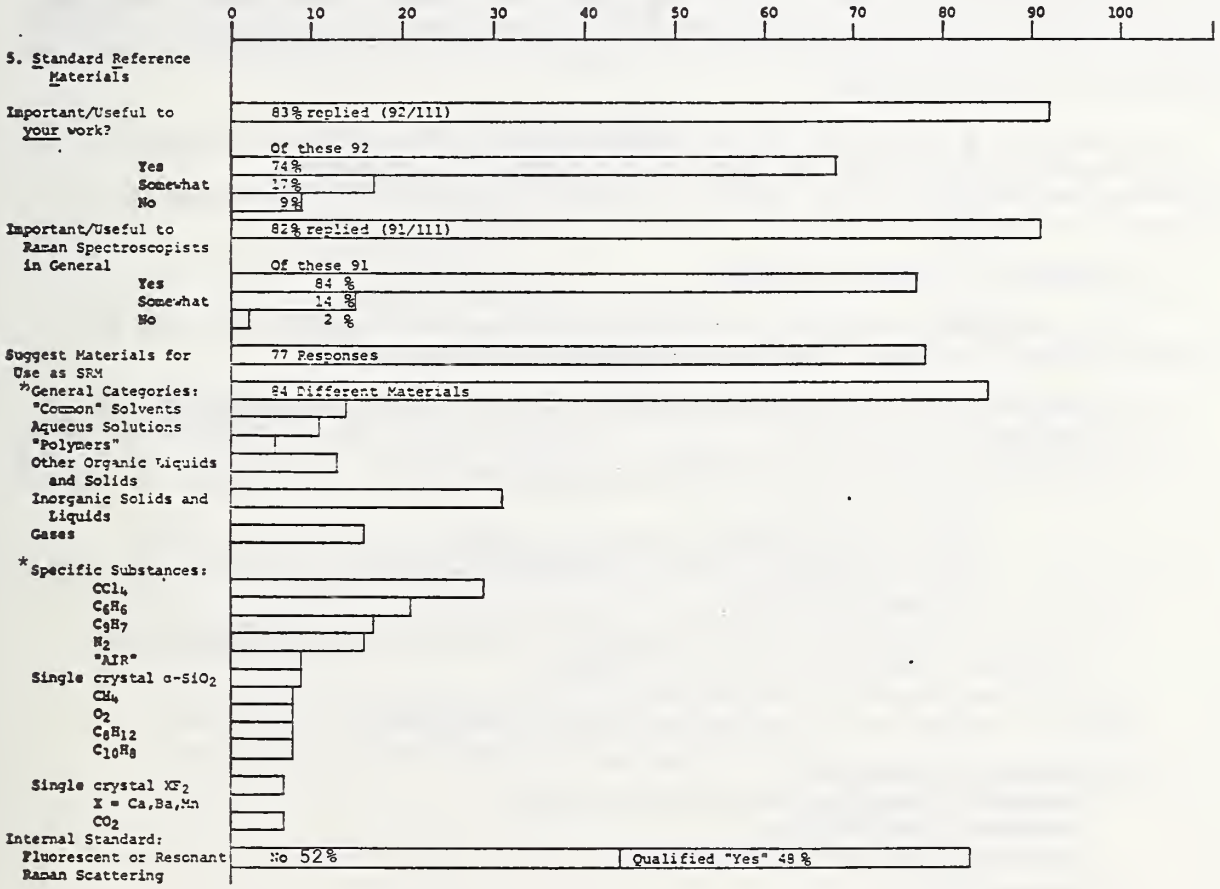

There are significant problems encountered in the comparison of Raman data from "other sources." Interestingly, a large number of respondents have encountered problems because the Raman frequency shifts are not accurately reported. Since accurate frequency calibration is generally a routine matter, this observation suggests that improvements in the data base can be achieved by spectroscopists being a little more conscientious.




There is definite interest in data cataloging efforts. In replying to the question of increased "efforts" in this area, many respondents cited "efforts" such as "systematization" and "standardization." There were warnings to avoid a repetition of the history of IR data cataloging ventures. The nature and importance of this problem are generally understood. These concerns have been communicated to a variety of groups whose activities involve "reference data."




This subject area was included in the questionnaire in order to assess the reaction to the "Recommendations"* and, further, to assess the need for simultaneous presentation of Raman and infrared data in data collections. The number of positive replies (34 of 111) is not large enough to allow a resolution of these questions.




*Raman Newsletter, No. 29, 1971.

The area of standard reference materials elicited strong, positive comment overall. A very important consideration which is not easily quantified "emerged" from the analysis of the survey. This consideration involves two problems: (1) How do we measure the standard spectrum of a standard reference material, and (2) how do we transfer the necessary measurement technology to the user of the SRM? The definition and/or development of this technology involves (1) accurate laser power measurement (at the sample), (2) selection of reproducible scattering geometry and laser focusing parameters, (3) accurate determination of collection and transfer efficiency of the fore optical system, (4) measurement of the spectrometer transfer efficiency, (5) measurement of the absolute detector response function, (6) measurement of the polarization character of the incident and scattered light, and (7) measurement and deconvolution of the spectral effects of the instrument function.

The use of standard reference materials will, hopefully, allow laboratories to measure a spectrum truly representative of the material without the need of performing all the calibrations listed above. The development and implementation of simple, accurate techniques for calibrations such as the above items are first priorities for establishing a useful standard reference material.

The information gained in this survey has been communicated to a number of organizations involved in standards for Raman spectroscopy. These activities are detailed in Section 3.8. Positive steps pursuant to the promulgation of useful standards for data presentation are being taken in cooperation with the Joint Committee on Atomic and Molecular Physical Data. Developments relevant to the measurement of the absolute detector response function (item 5 above) have been communicated to Raman spectroscopists. Progress in this area will follow the level of the developments described above. A round-robin test designed to establish the magnitude of the errors encountered in data comparisons is also recommended.

This survey is a first step for the National Bureau of Standards in its efforts to help promote standardization in Raman spectroscopy. It is important to continue interacting with the scientific community in the area of standardization for Raman spectroscopy.

## 3.2 DOMESTIC AND FOREIGN RESPONDERS

The questionnaire was sent to 285 people, 192 of these in the U.S.A., and 93 in Canada, Europe, and Japan. The list for mailing was assembled from:

1. Mailing list of the RAMAN NEWSLETTER obtained from the Optical Society of America,
2. "Users" lists from Raman instrument manufacturers:

   Spex Industries, Inc.
   Jarrel-Ash Division, Fisher Scientific
   Cary Instruments Division, Varian Associates
   Beckman Instruments

3. Lists of participants: The International Conference on Light Scattering in Solids, 1968 (New York); 1971 (Paris).

The U.S. mailing can be broken down into two categories:

A. national laboratories
   commercial/industrial research laboratories
   instrument manufacturers
   government agencies and laboratories

B. universities.

57% (110/192) of the surveys were sent to those in category A. We note also that there are 69 organizations represented in category A.

The total number of responders was 111 or 39%; 40% (76/192) of the U.S. mailing and 38% (35/93) of the remainder. Various estimates by the Raman Technical Group of the Optical Society of America concluded that there are from 500 to 800 Raman facilities in the world and from 250 to 400 Raman facilities in the U.S.A. Hence we have sampled roughly one-quarter to one-half of the domestic Raman facilities.

Under category A (government, industry, etc.) of the U.S. mailing, 37% (41/110) responded, whereas 43% (35/82) of those in the universities responded. The response by number of organization in category A was 48% (33/69). There was a significant response from those involved in the commercial design and manufacture of Raman instrumentation. The magnitude of the response (39%) is quite good, but even more important was the detail and quality of the completed questionnaires. The survey covered a broad range of topics. Being somewhat "free-form," it also attempted to elicit a great deal of individual response. The efforts of the responders to relate valuable information in many areas of their expertise and their eagerness in many cases to assist in standards efforts are very encouraging indications to the significance of a "standards" effort.

We enclose a copy of the questionnaire as figure 1 for the convenience of the reader.

### 3.3 FIELDS AND AREAS OF APPLICATION

Questions II.1.A and II.1.C assess the areas of scientific interest of the responders. These areas are best described by the set of descriptive titles most regularly named by the responders. (In many cases, one person mentioned more than one area.) The breakdown is as follows:

| | |
|---|---|
| Molecular physics and chemistry of gases, liquids and solids | 31 |
| Analytical chemistry | 29 |
| Physical chemistry | 29 |
| Solid state physics | 25 |
| Organic chemistry | 15 |
| Biochemistry/biophysics | 14 |
| Inorganic chemistry | 12 |
| Polymer physics and chemistry | 10 |
| Instrument manufacture/data cataloging | 8 |

The scientists involved in these areas of research utilize data from a great variety of experimental disciplines (Question II.1.B). Infrared spectra and structural data (x-ray, neutron, and electron diffraction) naturally predominate among those mentioned. NMR spectra are also widely employed.

The wide variety of physical, chemical and biological disciplines encountered in the responses to this question suggests:

1. The survey results should reflect the needs and interests of a great many scientists.
2. The inter-disciplinary nature of light scattering research and its wide application to problems in diverse areas.
3. The importance of a useful and meaningful data base for Raman spectroscopy.

Figure 1.

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APPROVAL EXPIRES JUNE 30, 1973

NBS-732
(1-73)

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

## STANDARDS FOR RAMAN SPECTROSCOPY QUESTIONNAIRE

**PART I** Please complete identification material below

| Name *(Last, First, Middle)* | Organization/Affiliation |
|---|---|
| | |

Address *(Street, City, State, ZIP)*

**PART II** Please answer the following questions

1A. To what areas of science and technology do you apply the techniques of Raman spectroscopy?

B. What other types of data do you utilize in conjunction with Raman spectroscopy?

C. What type of problem do you attempt to solve by means of Raman spectroscopy?

2. Do you encounter problems in comparison of spectra from other sources that you would trace to lack of proper standardization procedures? (e.g., inaccuracies in frequency calibration, depolarization ratios and relative intensities.)

3. Standard Reference Materials. These materials could be used in Raman instruments for frequency and intensity calibration, and possibly will allow determination of instrument functions.

A. How would you assess the importance of standard reference materials?

(1) to your specific efforts?

(2) for the users of Raman spectroscopy?

B. What type of standard materials would be most useful? Please suggest specific candidates (useful to you or useful in general) in each category.

(1) Gas

(2) Liquid

(3) Solid

CONTINUED

Figure 1 (continued)

C. Would you prefer an internal (trace additive) standard (e.g., a species which shows sharp line fluorescence or resonant Raman scattering)?

Any suggestions?

D. What types of sampling geometries and cells would you recommend? *(Please be as specific as possible.)*

E. In what form would the companion standard spectrum be most useful to you; graphical/digital/tabular?

4. Catalog of reference Raman spectra.

A. How would you assess the importance of a catalog of Raman spectra?

(1) to your specific efforts?

(2) to the efforts of scientists as a whole?

(3) what Raman spectral catalogs are you presently aware of?

B. Should efforts in this area be expanded?

C. What types of materials would be important? Please specify some important materials in each category.

(1) Solvents (laboratory and/or commercial)?

(2) Substrate, window and cell materials?

(3) Common gases (pollutants)?

(4) Important solids?

5. IUPAC has approved a set of "Recommendations for Presentation of Raman Spectra for Cataloging and Documentation in Permanent Data Collections" (Raman Newsletter, No. 29, May 1971).

A. Do you have additional suggestions for the format in which the data is presented, such as presentation of Raman and infrared data simultaneously?

B. Do you have a preference for graphical, tabular, or digital presentation of standard spectra?

CONTINUED

Figure 1 (continued)

6. Do you have suggestions concerning the need to generate Raman standard reference materials which can be used as standards in other fields of spectroscopy, chemical analysis, and physical measurements? *(Please be specific)*

Does this need for compatibility affect all types of Raman Standards?

7A. What specific problems must be overcome in order to

(1) define a standard spectrum?

(2) make it practically useful?

B. What suggestions can you offer to meet these difficulties?

8. In what capacity can the National Bureau of Standards be most useful to spectroscopists in an effort to establish standards for Raman spectra?

**PART III** We would appreciate any comments you may wish to add



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### 3.4 DATA BASE PROBLEMS

Question II.2 examines the magnitude of the problems encountered in comparison of Raman data from various sources. One hundred (90%) of the responders replied to this question and of these only 16% experienced "no" problems. In some of these cases, there were no problems because very little literature data was available with which to compare their data. The 84% who experienced problems cited a variety of types of inaccuracies. The following lists the problems and the number of times cited (more than one area was typically mentioned in a response):

| | |
|---|---|
| Accuracy (relative and absolute) of measurement of intensity of scattered light | 64 |
| Accuracy of frequency (shift) measurements (and in some cases also linewidth measurements) | 58 |
| Accuracy of determination of polarization properties | 51 |
| Incomplete specification of relevant experimental parameters and sample characteristics | 18 |

The responses to this question indicate that serious problems are encountered in the measurement and reporting of all the vital parameters of Raman spectrum. Some of these inaccuracies are primarily rooted in the difficult nature of certain measurements and calibration, e.g., intensity measurements and linewidth deconvolutions. It is somewhat surprising that frequency inaccuracies are encountered so often. This may stem from the fact that in many experiments accurate frequency values are not particularly important. An important inference is that the problem areas cited by the responders may in many cases be remedied by selecting standard techniques and reference materials.

### 3.5 STANDARD REFERENCE MATERIALS

Question II.3 addresses the use of Standard Reference Materials, described in the questionnaire by: "These materials could be used in Raman instruments for frequency and intensity calibration, and possibly will allow determination of instrument functions." The question of the importance of SRM's to "your specific efforts" (Question II.3.A.1) and "for the users of Raman spectroscopy" (Question II.3.A.2) was answered as follows:

To Question II.3.A.1, 83% (92/111) replied, and of these 74% (68/92) thought that an SRM would be important or very important to their work, 17% (16/92) saw some importance, and 9% (8/92) said not important.

To Question II.3.A.2, 82% (91/111) replied, and of these 84% (76/91) thought that an SRM would be important or very important to users in general, 14% (23/91) saw some importance, and 2% (2/91) said not important.

Many responders used the word "useful" and the word "important" should be understood in this context.

Question II.3.B asks for specific candidates for reference materials. A number of responders emphasized that frequency calibration is "best" accomplished by means of "known" atomic standards, i.e., Ne, Ar, Kr lamps, or possibly the non-lasing emission lines from the laser plasma. The important characteristics (spectral properties and

material properties) of a standard reference material were outlined by others (20-30 responders). Such characteristics were also mentioned in response to Questions II.7.A&B. For example, the Raman spectrum of the material should exhibit strong, sharp lines, cover a wide frequency range, and be insensitive to temperature and excitation wavelength. The material itself should be non-toxic, non-hygroscopic, easy to purify and easy to measure.

Seventy-seven (77) of the responses included some specific recommendations for a reference material. In the remaining portion of this paragraph the numbers in parentheses represent the number of times a material was cited. Eighty-four different substances were named in the categories of common solvents (12), aqueous solutions (10), polymers (5), "other" organic liquids and solids (12), inorganic liquids and solids (30), and gases (15). Some frequently mentioned compounds were: $CCl_4$ (28), $C_6H_6$ (20), $C_9H_7$ (Indene) (16), $N_2$ (15), "Air" (8), single-crystal $\alpha$-$SiO_2$ (8), $CH_4$ (7), $O_2$ (7), $C_6H_{12}$ (7), $C_{10}H_8$ (Napthalene) (7), single-crystal $XF_2$ (X = Ca, Mn, Ba) (6), and $CO_2$ (6). In many cases the "popular" materials do not display some of the important characteristics of a "reference" material. A set of "best" candidates has not emerged from the evaluation of the survey.

Question II.6 addresses the need for compatibility of reference materials among the various physical and chemical disciplines. Only 20% (22/111) of the responders commented on the need for compatibility. From these answers there was no strong indication of the necessity to design strictly compatible standards although such efforts "might be helpful."

Question II.3.C&D explored two further areas with regard to reference materials. The possibility of using a "trace" additive internal standard was the subject of Question II.3.C. The trace additive standard, which was suggested in the question, might display either sharp-line fluorescence or resonant-Raman scattering. There were several objections to the use of fluorescent or resonant standards; namely, the strong wavelength dependence, unknown solvent effects, and some basic uncertainties with regard to the nature of the effect in the case of resonant scattering. Objections were also raised because of possible chemical interferences. Over-all, then, 52% of the 83 responses were against the idea of an "internal" standard. The remaining 48% gave a qualified yes.

Part D of Question II.3 addressed the problems of sample cells and scattering geometry. There were 69 responses to this question. 90° geometry was suggested 50 times vs. 13 suggestions of 180° scattering. Capillary tubes (melting point type) were suggested 23 times as sample cells for liquids. Cylindrical cells illuminated along their axes (8 responses) and rectangular cells (7 responses) were mentioned among the other "popular" cells. Single pass was explicitly mentioned ten times and multi-pass in five responses.

### 3.6 REFERENCE DATA

In Question II.4 the survey attempted to assess the present level of interest in data cataloging efforts in the field of Raman spectroscopy. The results of these inquiries are as follows:

Question II.4.A.1 Are data catalogs important to your specific efforts?

> 83% (92/111) indicated that the catalogs were important or very important; 17% (16/92) said "some importance"; and 23% (21/92) indicated "not important."

Question II.4.A.2 Are the data catalogs important to users of Raman spectroscopy in general?

78% (87/111) commented; 78% (68/87) of those who commented said important or very important; and 22% (19/87) said "some importance."

This question -- II.4.A.3 -- also asked the responder to name the catalogs of Raman spectra of which he was aware. 83% (92/111) commented. The results were as follows: 25%, none; 37%, one; 21%, two; 17%, three or more. In this question the responders mentioned the very limited editions of certain instrument manufacturers.

The subject of Question II.4.B was need for further efforts in this area. 75% (83/111) commented; and of these 95% (79/83) felt that these "efforts" should be expanded. However, the nature of these "efforts" was, in many cases, suggestions to "organize," "systematize," and "evaluate" the spectral catalogs. A significant number of comments concerned the need to avoid proliferation, duplication, and incompatibility of the cataloging efforts in Raman spectroscopy.

Question II.4.C. asked for specific candidate materials for spectral cataloging. The response to this question was not as large as for the similar question with regard to SRM's (II.3.B). There was a large variety in the responses with no trends.

### 3.7 FORMATS FOR RAMAN DATA PRESENTATIONS

Question II.5 concerned the recently published (IUPAC approved) "Recommendations for Presentation of Raman Spectra for Cataloging and Documentation in Permanent Data Collections." We asked for additional suggestions for the format of the data and, in particular, questioned if the Raman and infrared formats should be identical and if the "Permanent Data Collections" should present both the Raman and infrared spectra of a compound. 58% (65/111) responded to the question and of these 48% (31/65) had no additional suggestions. Fifteen types of suggestions were made; the most significant of these was: 17 people wanted compatible IR-Raman formats whereas 5 were against this position (or at least wanted some changes in the 0-400 $cm^{-1}$ region); 5 people wanted the spectra presented after correction for instrumental effects. Our impression is that many of those who returned the questionnaire were not aware either of the "Recommendations" or of their intent.

The comments associated with Question II.6 are included in the discussion of Question II.3.

### 3.8 PROBLEM DEFINITION AND RESEARCH STRATEGY

Question II.7 is extremely vital to the evaluation of any efforts to provide a standard reference spectrum of a standard reference material. The comments on the nature of the material chosen as a standard have been included under the discussion of Question II.3. The important conclusion to be drawn from the answers to Question II.7 and throughout relevant sections of the questionnaire is that there are fundamental problems involved in the measurement of a "standard" spectrum, i.e., a spectrum truly representative only of the material, not of the instrument used to make the measurements. This latter requirement is essential to the definition of a standard reference material. This problem area will be dealt with in the summary of options discussed below.

Question II.8 asked "In what capacity can the National Bureau of Standards be most useful to spectroscopists in an effort to establish standards for Raman spectra?" The responses to this question and many comments from other parts of the questionnaire are relevant to the choice of directions to be pursued by the National Bureau of Standards and others concerned with standards efforts. These responses can best be discussed under two headings: I. Assuring efficient production of (commercial) spectral catalogs, and II. Proceeding toward the generation of standard reference spectra.

Under heading I, there were a wide variety of recommendations. Some of these have been discussed in question II.4.B. It is suggested that a classification of Raman spectra along the same lines as the Coblentz designations IR - I, II, III would be appropriate for spectral catalogs and standard reference spectra. The production and distribution of commercial spectral catalogs is seen as important by the responders. However, these catalogs must be extensive to be useful and at the same time inexpensive to produce if they are to be practical for both the producer and purchaser. Thus, they would generally fall into a category similar to Coblentz IR-III. The responders were generally in agreement that, within the limits of this class, efforts should be directed toward assuring the maximum, practical quality of the data (sample quality and spectral quality). Relevant spectral parameters must be specified (see discussion below), and the format of presentation should be uniform both within a data compilation and for different compilations. The specification of relevant spectral parameters and questions of format for data presentation have been addressed in the "Recommendations" of the Raman subcommittee of the Joint Commission on Atomic and Molecular Physical Data (NSRDS) and approved by IUPAC. At least a minimal subset of these recommendations should be adopted as a uniform requirement for Class III collections. As mentioned above, there is a need to "organize," "systematize," and "standardize" data catalogs. The Bureau is seen by the responders as having varying degrees of responsibility towards realization of these goals. The concerns of the responders have been communicated to the Raman Technical Group of the Optical Society of America (Spring Meeting, Denver, Colorado, March 1973) and have been discussed with the chairman of the Raman Technical Group; Dr. Ted Becker, National Institutes of Health, Chairman of the Raman Committee of the Coblentz Society; and Dr. Stephen Rossmassler, National Bureau of Standards, Office of Standard Reference Data.

Recently, at the September 12, 1974, meeting of the Executive Committee of the Joint Committee on Atomic and Molecular Physical Data, the topic of standards for Raman data presentation was addressed. The results of this survey were presented as part of the meeting agenda. As a result of this interaction, G. Rosasco, with the consultation of the JCAMPD and a panel of Raman experts, will be preparing a manuscript which will serve to establish a preferred set of specifications for Raman data presentation.

Concerning heading II, the results of the survey generally are positive on the usefulness of determining standard reference spectra (of standard reference materials), and indicate a definite role for NBS in such an effort. The areas of effort are:

(1) Specification of standards and techniques for calibration of frequency, intensity and instrument response functions.

(2) Development, evaluation, and recommendation of standard methods for obtaining reference quality (Class II and I) spectra.

(3) Selection, measurement, and distribution of reference spectra of reference materials.

The order of importance (and frequency) of suggestion is as numbered above. This order is based on a systematic approach to the standardization problem and thus constitutes a reasonable framework for structuring a measurement strategy. Within this strategy provision should be made for multi-lab measurements of "standard" samples; this point was raised by a number of responders, and, in fact, some volunteered to cooperate in such an effort.

In the context of a research strategy based essentially on items (1) through (3), some initial efforts are under way by G. Rosasco in search of spectroscopic standards and techniques for frequency and intensity calibration. As an example of this effort, we are inquiring into Bureau calibration of radioactively pumped phosphors as intensity

standards. The present intensity standard is a photometric standard whose specific properties and certain concomitant difficulties in technical procedures (and high cost) cause it to be less than ideal for routine standardization of Raman spectrometers.

The experimental procedures to be addressed in item (2) involve questions as to laser power measurement, determination of polarization properties of incident and scattered light, and techniques for measurement and deconvolution of the effects of instrument functions of Raman spectrometers. G. Rosasco visited the NBS Boulder Laboratories in March 1973 specifically to learn more about accurate laser power measurement. We have informed Raman spectroscopists via the RAMAN NEWSLETTER (August 1973) of the Bureau's efforts (in conjunction with the ASTM Committee F-1.02) in a Measurement Assurance Program for laser power measurements. G. Rosasco is attempting to keep abreast of developments at NBS (Boulder) and from ASTM F-1.02 in order to inform Raman spectroscopists.

Within the context of item (2), it appears useful for NBS to communicate significant information from the "experts" in an associated problem area to Raman spectroscopists. The "experts" in many cases will come from the field of Raman spectroscopy, and in any selection of a "standard" technique the particular needs of Raman spectroscopists must be considered. These efforts seem appropriate for NBS and follow from a significant number of suggestions from the responders.

A natural evolution from significant achievements under items (1) and (2) would be specific efforts on the part of NBS and other interested parties toward fulfillment of item (3). There are a variety of strategies one can apply to the selection of reference materials. Because of the many interests of Raman spectroscopists, it may be necessary to select a number of materials. In some cases a "material" may have to be defined, e.g., a mixture of liquids or gases. A list of minimum requirements for a reference material should be selected and possible candidates chosen. In this process the experts in each area (gas phase, aqueous solutions, etc.) should be consulted. Careful evaluation of the candidates should be made by a group of Raman spectroscopists; for example, the Advisory Board of the RAMAN NEWSLETTER.

In addition to a role in the communication of important developments towards the realization of "standards" for Raman spectroscopy as outlined above, another important contribution could be made at this time. This effort would be a first round of multi-lab testing of a selected sample for the purposes of evaluation of routine Raman measurements. This idea evolved from a discussion at the Spring 1973 meeting of the Raman Technical Group. A number of variations to the nature of the test were suggested. However, a simple, straightforward test specification seems most useful at this point. The procedure for the multi-lab test seems relatively straightforward and G. Rosasco is willing to implement the testing, i.e., sample preparation, distribution and compilation of results. Further details will be specified after the basic concept is approved.

This development sequence is based on the knowledge of problem areas related to Raman spectroscopy. Solution of each level of problem and an adequate evaluation of routine test spectra will be invaluable to the design, measurement and successful implementation of a standard reference material.

# 4.0 SURVEY REPORT ON STANDARDS FOR ELECTRON PARAMAGNETIC RESONANCE

## 4.1 INTRODUCTION

We report here the findings of our survey-questionnaire to assess the need for a standard reference material (SRM) by which to improve intensity measurements in electron paramagnetic resonance (EPR). This report summarizes the requirements of the potential users of EPR SRM's and reveals possible areas of difficulties where we may render technical assistance.

Table 1 gives an analysis of the survey sampling. The list for mailing was assembled from the mailing list of an EPR spectrometer manufacturer and from our own contacts. We enclose a copy of the questionnaire as figure 2. We sent out 518 questionnaires. Of this number 15 either were returned by the Post Office as not deliverable or were sent to persons who are no longer performing EPR measurements. We therefore take 503 as the base number. The number of answered questionnaires is 175. This is 35% (175/503) of the base number. We received answers from 24 different companies, 26 different government laboratories, and 90 different universities.

Table 1. Analysis of Sampling

| | Number |
|---|---|
| Total number of questionnaires sent out | 518 |
| Returned by Post Office as not deliverable | 13 |
| No longer in EPR | 2 |
| Base number of questionnaires sent out | 503 |
| Answered questionnaires | 175 (35%) |

We estimate that there are about 1000 EPR groups in the world, and that the number of domestic EPR groups is between 400 and 500. Most of the foreign EPR groups listed in Table 1 are from Europe, Canada, and several from Japan, Australia, and South America. We did not reach east European countries, Russia, China, India, or Arabia. We know of several groups in these countries.

The background of the responders is given in Table 2. We prepared Table 2 from our knowledge of the organizations of the responders. We divide the EPR users into three major disciplines; namely, physics, chemistry, and biomedicine. For this analysis we place biologists, medical researchers, and pharmacists in the biomedical category. We recognize that some physicists and chemists also work on biological problems. Thus, one quarter of the EPR users is in physics, one quarter is in biomedicine, and the remaining half is in chemistry. We find by reference to the journals in which researchers in physics and biomedicine publish that there is a trend for the number of EPR users in biomedicine

Figure 2.

OMB NO. 41-S72080
APPROVAL EXPIRES JUNE 30, 1973

NBS-896
(9-72)

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

## QUESTIONNAIRE FOR ELECTRON PARAMAGNETIC RESONANCE (EPR) STANDARD REFERENCE MATERIALS

TO:

PLEASE RETURN THIS QUESTIONNAIRE TO

Dr. Te-Tse Cheng
National Bureau of Standards
Bldg. 223, Room A-259
Washington, D. C. 20234

1a. Do you think National Bureau of Standards certified EPR standard reference materials are needed? ☐ YES ☐ NO

b. If no, disregard the following questions and return the questionnaire

2a. Have you ever attempted to measure the number of spins in your experiments? ☐ YES ☐ NO

b. If yes, what reference sample did you use?

c. How accurate and precise was the reference sample you used? Accuracy _____ % Precision _____ %

d. If the experiments are described in any publications, please send a reprint, or cite reference

3. If you were purchasing a set of EPR standard reference materials, list your preference for the following:

| a. shape | b. size | c. concentration range of paramagnetic ions |
|---|---|---|
| | | |

d. Within what temperature range would you use the EPR standard reference materials?

e. List frequency band(s) you:

| (1) now operate in | (2) expect to operate in, in the future |
|---|---|
| | |

f. How accurate would you want the EPR standard reference materials to be?

4. Any additional comments would be welcomed

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to increase and for the number of EPR users in physics to decrease.

Table 2. Background of Responders

| Physics | Chemistry | Biomedicine | Not determined | Total |
|---|---|---|---|---|
| 35 | 71 | 29 | 40 | 175 |

## 4.2 FINDINGS AND DISCUSSION

### 4.2.1 Question 1 -- Need

Question 1 assesses the need for EPR standard reference materials. Table 3 shows that 93% (163/175) of the responders answered "yes." Hence the EPR community needs and wants a standard reference material.

Table 3. Is a National Bureau of Standards certified SRM for EPR needed?

| | U.S.A. | Foreign | Total | Percent |
|---|---|---|---|---|
| Yes | 121 | 42 | 163 | 93% |
| No | 10 | 2 | 12 | 7% |

### 4.2.2 Question 2 -- Present Reference Samples

Question 2 concerns the existing samples by which EPR users measure line intensities. These samples are not calibrated nor certified. They estimate the spin concentration by knowing the weight of the sample and its chemical composition.

Table 4 shows that 87% (129/157) of the responders to question 2 tried some quantitative EPR measurements. Everyone who attempted quantitative EPR measurements mentioned that the lack of standards presents great handicaps and difficulties. Among those who had not attempted quantitative EPR line intensity measurements, some stated that they plan to do so in the near future. Others stated that they cannot make quantitative line intensity measurements because there are no standards. The general assessment is that a good standard reference material is necessary for EPR intensity measurements.

Table 4. Quantitative Measurement Attempted

| | U.S.A. | Foreign | Total |
|---|---|---|---|
| Yes | 96 | 33 | 129 |
| No | 20 | 8 | 28 |

Table 5 lists the commonly used reference samples in order of the number of times each sample was cited. In order to shorten this table we have combined some of the entries. For example, the item "copper salts in various forms" represents

$CuSO_4$, $CuCl_2$, and other Cu bearing salts in single crystal, powder, or solution forms. The copper content of such samples may also be diluted. This table shows that convenience and availability are important factors in selecting reference samples.

Table 5. Existing Reference Samples

| Reference Sample | Number of times cited |
|---|---|
| DPPH | 53 |
| Pitch in KCl and Varian samples | 37 |
| Cu salt in various forms | 37 |
| Mn salt in various forms | 16 |
| Various free radials (except DPPH) | 16 |
| Spin label, in various forms | 14 |
| P-doped Si (Bell Laboratories sample) | 8 |
| Charcoal (including radiated carbon, burned sugar, etc.) | 6 |
| $VO^{++}$ in various forms | 4 |
| Ruby or Cr ions in various forms | 4 |
| $O_2$ | 2 |
| F-center in KCl | 1 |
| $Fe^{+++}:Al_2O_3$ | 1 |

Table 6 presents the assessments by the responders themselves of the accuracy and precision of their present reference samples. This table shows that a standard reference sample which results in EPR line intensity measurements accurate and precise to within 10% will satisfy the present needs for over half of the responders. In addition, comments on the answered questionnaires, follow-up conversations with some of the responders, and this Table 6 all indicate that we must educate some of the potential users of EPR SRM's to understand the difference between accuracy and precision.

Table 6. Quality of Existing Reference Samples

| Percent accuracy or precision stated by responders | Number of times cited for Accuracy | Precision |
|---|---|---|
| 0.1% to 4.9% | 14 | 15 |
| 5.0% | 17 | 17 |
| 6.0% to 14.9% | 25 | 19 |
| 15% to 50% | 8 | 24 |
| greater than 50% | 2 | 11 |
| Responders stated that accuracy and precision for the number of spins is: | | |
| Not known | 14 | 16 |
| Poor | 4 | 4 |
| Known to an order of magnitude | 6 | 6 |

If the EPR spectrometer has reliable and stable units, and if the experimental conditions are kept the same or are monitored for changes and the data are corrected accordingly, the reproducibility of the EPR measurements may be precise to within 1%. This is good precision but the correlation of the experimental results with the true number of spins is not straightforward, particularly when the correlation is not well defined. Also, very accurate reference samples may be prepared, but transferring this accuracy to the EPR measurements may not be achieved readily. For example, the $CuSO_4$ solution may be prepared with a concentration known to a ±0.01% accuracy; however, the transfer of this accuracy becomes questionable when the solution is placed in a quartz tube and inserted into the microwave cavity without additional precautions. The manners in which the reference sample and the unknown sample perturb the electric and magnetic fields of the cavity must be determined first. That is, the user must know what quantity is being measured.

4.2.3 Question 3 -- Sample Characteristics

Question 3 considers the shape, size, and concentration range of paramagnetic ions, temperature range, and frequency range. Table 7 summarizes the shapes and sizes which the responders preferred. The item "cylinder" in this table includes also rods and tubing. The item "cube" includes cubes, squares, rectangles, and needles. Because most users place samples in quartz tubes, they would prefer a cylindrical standard sample. Most responders want sample standards 4 mm in size or smaller, so that placing the standards near the unknown sample in the cavity does not disturb the measurement. The second largest number requested cube-shaped samples. We conclude that EPR SRM's which are small cylinders or cubes will satisfy the needs of most people.

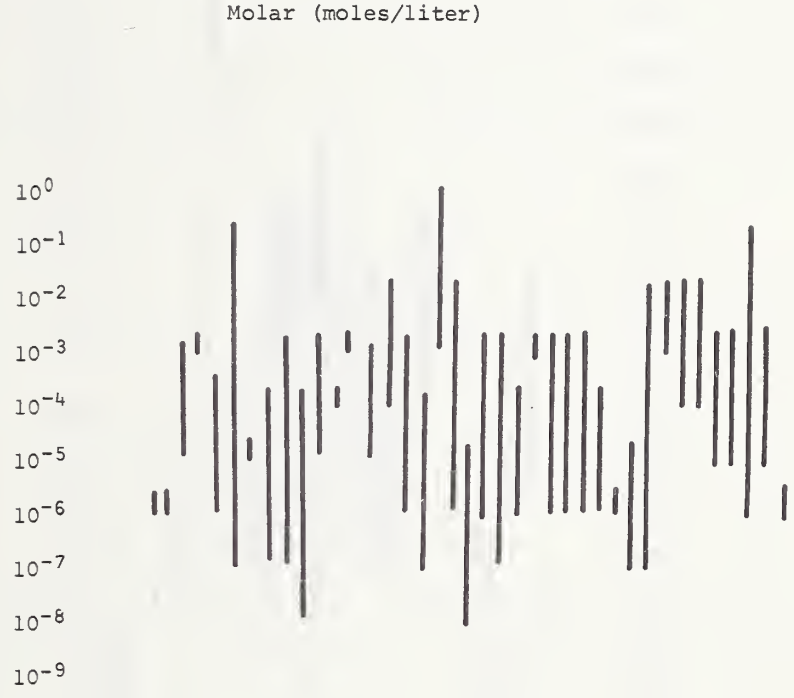
Table 7. Shape or Form

| | Number of Times Cited |
|---|---|
| Cylinder | 77 |
| Cube | 21 |
| Single crystal | 9 |
| Powder | 17 |
| In solution | 7 |

Size -- 4 mm or smaller

Figures 3 to 6 are bar graphs and illustrate the distributions of concentration ranges for the paramagnetic ions (spins) expressed by the responders. Each figure corresponds to one of the several ways in which responders expressed the concentration. Each vertical bar in these figures represents the range of concentrations requested by an individual responder. The average value for the concentration in the mole/liter (figure 3) is about $5 \times 10^{-5}$ moles/liter. If we use a quartz tube with a 2-mm inside diameter in a 25-mm length, the volume is about $0.8 \times 10^{-4}$ liters and the number of paramagnetic ions is in the $1 \times 10^{15}$ range. The average number for the paramagnetic ions in each of the remaining three figures is also about $10^{15}$. Hence, from these data we conclude that the first EPR SRM to be issued should contain about $10^{15}$ spins and that succeeding EPR SRM's should then possess concentrations both greater and lower than this value.

Figure 3. Molar concentration of paramagnetic ions




Each vertical line represents the range of concentration requested by an individual responder.

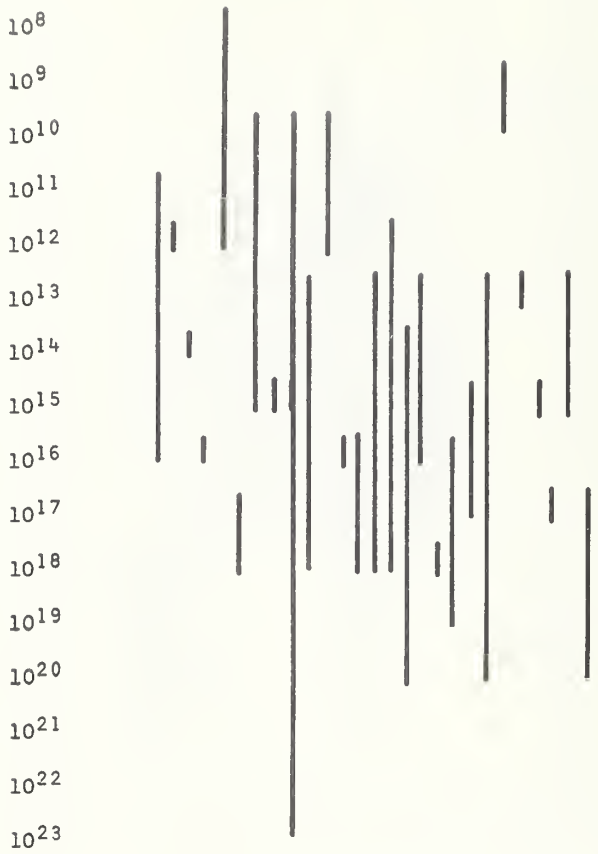
Figure 4. Number of spins/gm


Each vertical line represents the range of number of spins per gram requested by an individual responder.

Figure 5. Number of spins/$cm^3$


Each vertical line represents the range of the number of spins per cubic centimeter requested by an individual responder.

Figure 6. Total number of spins in sample




Each vertical line represents the range in the total number of spins requested by an individual responder.

Most responders stated that we should provide the most accurate sample possible. Our present knowledge and experience suggest that our first goal be an SRM which is 20% to 50% accurate. In the future we should work towards the 5% to 15% range indicated by the survey.

### 4.3 ADDITIONAL COMMENTS

Most of the answered questionnaires contained enthusiastic comments. Some responders also offered to assist us, and others were pleased that someone finally is engaged to develop an EPR SRM.

The analysis of the answers to this questionnaire establishes that the EPR community needs standards. The first standard could be a single crystal in the shape of a cylinder or cube which is small enough to fit into 4-mm inside-diameter tubing and which has about $10^{15}$ spins. We should consider later issuing other concentrations and other sizes and exploring alternative materials for standards. We should develop continuing research and calibration efforts. And, finally, the purchasers of EPR SRM's should be provided with technical help and advice, and, particularly as indicated by Tables 2 and 6, with detailed and extensive instructions on how to use EPR SRM's.

# 5.0 SURVEY REPORT ON STANDARDS FOR MAGNETIC MOMENT MEASUREMENTS

### 5.1 INTRODUCTION

At present, there are no reliable and accurate standard calibrants for magnetic moment measurements. For this reason, we at NBS are considering the preparation and certification of a Standard Reference Material (SRM) for magnetic moment. In order to assess the need and to determine the characteristics for such a standard reference material, we have undertaken a survey-questionnaire. Figure 7 is a copy of the questionnaire.

During October 1974, 781 questionnaires were mailed to addresses in the United States. These addresses were obtained from the mailing list maintained by the American Institute of Physics for the annual Conference on Magnetism and Magnetic Materials. In this report the following classification is used: industry, university, government, private individual, and unknown. The classification "unknown" is for those questionnaires which were returned without a name or address on them.

Table 8 shows the mailing distribution of the questionnaire.

Table 8. Mailing Distribution

| Classification | Number | Percentage |
|---|---|---|
| Industry | 337 | 43 |
| University | 276 | 35 |
| Government | 116 | 15 |
| Private | 52 | 7 |
| Total | 781 | 100 |

Figure 7.

OMB 41-S74077
APPROVAL EXPIRES: JUNE, 1975

NBS-794
(9-74)

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

## QUESTIONNAIRE FOR MAGNETIC MOMENT STANDARD REFERENCE MATERIALS

TO:

PLEASE RETURN THIS QUESTIONNAIRE TO:

OFFICE OF STANDARD REFERENCE MATERIALS
CHEMISTRY BLDG., ROOM B311
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C. 20234

(A PRE-ADDRESSED, POSTAGE-PAID ENVELOPE IS ENCLOSED FOR YOUR CONVENIENCE.)

THE NATIONAL BUREAU OF STANDARDS IS PROPOSING TO PREPARE AND CERTIFY A STANDARD REFERENCE MATERIAL (SRM) FOR MAGNETIC MOMENT. THE PROPOSED SRM IS FOR A 3MM-DIAMETER NICKEL SPHERE CERTIFIED FOR SATURATION MAGNETIZATION AT ROOM TEMPERATURE TO WITHIN ± 5 PERCENT ACCURACY.

THE PURPOSE OF THIS QUESTIONNAIRE IS TO DETERMINE THE EXTENT OF THE NEED FOR SUCH AN SRM. BECAUSE QUESTIONNAIRES MAY NOT REACH ALL INTERESTED PARTIES, YOU ARE ENCOURAGED TO SUBMIT THE NAMES OF COLLEAGUES WHOM YOU FEEL WOULD WISH TO RECEIVE THE QUESTIONNAIRE.

1. DO YOU NEED A STANDARD REFERENCE MATERIAL FOR MAGNETIC MOMENT TO CALIBRATE MAGNETOMETERS? ☐ (A) YES ☐ (B) NO ☐ (C) NOT IN MY FIELD OF INTEREST

IF (B) OR (C), DISREGARD THE FOLLOWING QUESTIONS AND RETURN THE QUESTIONNAIRE

2. DO YOU NOW USE A CALIBRANT WITH YOUR APPARATUS? ☐ (A) YES ☐ (B) NO

IF "YES," PLEASE ANSWER THE FOLLOWING QUESTIONS:

(A) WHAT CALIBRANT DO YOU USE?

(B) IS YOUR APPARATUS ADAPTABLE TO VARIOUS SIZES OF SAMPLES? ☐ (A) YES ☐ (B) NO

(C) WHAT IS THE MAXIMUM MAGNETIC FIELD OBTAINED WITH YOUR MAGNET?

(D) PLEASE CITE THE REFERENCES THAT DESCRIBE YOUR EXPERIMENTS, OR SEND REPRINTS.

Figure 7 (continued)

3. PLEASE LIST YOUR PREFERENCES FOR AN SRM FOR MAGNETIC MOMENT.

- ☐ (A) SHAPE (IF OTHER THAN SPHERICAL)
- ☐ (B) SIZE
- ☐ (C) MATERIAL
- ☐ (D) ACCURACY (IF BETTER THAN ± 5%)
- ☐ (E) MAGNITUDE OF MAGNETIC MOMENT
- ☐ (F) TEMPERATURE (OTHER THAN ROOM)
- ☐ (G) OTHER SPECIFICATIONS (LIST)

4. IF THE PROPOSED SRM (3MM-DIAMETER NICKEL SPHERE) WERE AVAILABLE FOR APPROXIMATELY $150, WOULD YOU PURCHASE IT? ☐ (A) YES ☐ (B) NO

5. PLEASE LIST THE NAMES AND ADDRESSES OF ANY PERSONS YOU FEEL WOULD BE INTERESTED IN AN SRM FOR MAGNETIC MOMENT.

ADDITIONAL COMMENTS

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Table 9 lists the returns as of December 2, 1974.

Table 9. Returns

| Classification | Number of Returns | Normalized Returns: Number of Returns | Normalized Returns: Percent of Number Sent Out (Table 8) | Normalized Returns: Relative Percent |
|---|---|---|---|---|
| Industry | 69 | 120 | 36 | 40 |
| University | 71 | 124 | 45 | 42 |
| Government | 22 | 38 | 33 | 13 |
| Private | 9 | 15 | 33 | 5 |
| Unknown | 126 | - | - | - |
| Total | 297 | 297 | | 100 |

We have normalized the returns by assuming the 126 unknown returns have the same distribution among classifications as those returns with a name or address on them. Both in number and percentage, a slightly larger response was obtained from universities.

5.2 DATA BASE AND FINDINGS

In this report, each question will be stated, followed by a summary of the response to it, and then analyzed.

Question 1. Do you need a standard reference material for magnetic moment to calibrate magnetometers?

(A) Yes (B) No (C) Not in my field of interest

Table 10. Response to Question 1

| Classification | Number of Returns: Yes | No | Not in my field of interest |
|---|---|---|---|
| Industry | 35 | 25 | 9 |
| Universities | 38 | 18 | 15 |
| Government | 9 | 5 | 8 |
| Private | 2 | 2 | 5 |
| Unknown | 40 | 43 | 43 |
| Total | 124 | 93 | 80 |
| Percent of response | 42 (124/297) | 31 (93/297) | 27 (80/297) |
| Percent of those in field | 57 (124/217) | 43 (93/217) | |

A majority (57%) of the responses from workers in the field claims that a need for an SRM exists. The remainder of this report will analyze the 124 questionnaires on which the response to question 1 was yes.

Question 2. Do you now use a calibrant with your apparatus?

Yes No

Yes - 103 No - 16 Percent Yes - 87

Of the 124 who claimed they need an SRM, 103 or 83% already are using a calibrant. This response and that to Question 1 indicate that these workers are not completely satisfied with their own reference material and would like an SRM certified by a reputable standards laboratory.

Question 2, continued

If "Yes," please answer the following questions:

2A. What calibrant do you use?

Table 11. Response to Question 2A

| | Number | Percent of Total |
|---|---|---|
| Ni | 78 | 60 |
| Area-turns | 15[a] | 12 |
| Paramagnetic salts | 11[b] | 9 |
| Fe | 8 | 6 |
| Ferrites | 5 | 4 |
| Iron oxides | 4 | 3 |
| Superconductors | 4 | 3 |
| Others | 4[c] | 3 |
| Total | 129 | |

[a]Includes reference magnets (5), reference voltage (1)
[b]Persons informed of existing SRM's for paramagnetism
[c]Pb, Ge, Ta, Mo

The majority of those who use a calibrant use nickel.

2B. Is your apparatus adaptable to various sizes of samples?

Yes No

Yes - 98 No - 12

Although 89 percent (98/110) answered yes to this question, a size preference is shown later in question 3B.

2C. What is the maximum field obtained with your magnet?

Table 12. Response to Question 2C

| Field (tesla) | Number | Percent of Total |
|---|---|---|
| 0 - 0.1 | 7 | 6 |
| 0.1 - 0.5 | 9 | 7 |
| 0.5 - 1.0 | 25 | 21 |
| 1.0 - 2.0 | 34 | 28 |
| 2.0 - 3.0 | 17 | 14 |
| 3.0 - 5.0 | 7 | 6 |
| 5.0 - up | 22 | 18 |
| Total | 121 | |

Most of the fields above 3 teslas are produced by superconducting magnets. Approximately 13% of the responses need a moment characterized in a field of less than 0.5 tesla.

2D. Please cite references that describe your experiments, or send reprints.

| | |
|---|---|
| References cited | 51 |
| Reprints sent | 22 |

The responses from questions 2A and 2D show that the majority of the workers (124) are active in the field of magnetism.

Question 3. Please list your preferences for an SRM for magnetic moment.

There are seven parts to this question (A-G). These are discussed separately.

3A. Shape (if other than spherical)

Table 13. Response to Question 3A

| Shape | Number | Percent |
|---|---|---|
| sphere* | 96 | 72 |
| cylinder | 20 | 15 |
| film or disc | 15 | 11 |
| ellipsoid | 3 | 2 |
| Total | 134 | |

*Includes those who wrote in sphere (22) and those who left 3A blank. See questions 2A and 4. The vast majority chose a sphere which is easy to fabricate and whose demagnetization factor is well established.

3B. Size

Table 14. Response to Question 3B

| Size (diameter mm)* | Number | Percent |
|---|---|---|
| 1 | 9 | 16 |
| 2 | 15 | 27 |
| 3 | 20 | 36 |
| 4 | 4 | 7 |
| 5 | 4 | 7 |
| 10 | 4 | 7 |
| Total | 56 | |

*Only the size for a sphere has been tabulated.

More than one size sphere may be needed to satisfy the requests.

3C. Material

Table 15. Response to Question 3C

| Material | Number | Percent |
|---|---|---|
| Ni | 38 | 75 |
| Fe | 6 | 12 |
| Other* | 7 | 13 |
| Total | 51 | |

*$Fe_2O_3$ (2), nonmetallic (2), ferrite (1), Permalloy (1), superconductor (1).

There was a low response to this question; however, question 2A showed that most workers used nickel.

3D. Accuracy (if better than ±5 percent)

Table 16. Response to Question 3D

| Accuracy (%) | Number | Percent |
|---|---|---|
| .1 - .5 | 12 | |
| .6 - 1.0 | 30 | 49 |
| 1.1 - 4.0 | 16 | |
| 4.1 - 5.0 | 61 | 51 |
| Total | 119 | |

This is a very important question and clearly shows that about one-half of the workers would like an SRM certified to better than ±5 percent accuracy. One notes that our high

response for a ±5 percent accuracy may have been prejudiced by our phrasing of the question. However, the responses to question 4 and the additional comments given below indicate that a ±1 percent SRM is needed.

3E. Magnitude (emu/g)* Number

| | |
|---|---|
| < .1 | 10 |
| > .1 | 12 |

Only 22 persons answered this question, but it appears from other questions about materials that the majority of the workers need an SRM with a moment > .1 emu. (See questions 2A, 3C, and 4. Also note that the saturization magnetization for nickel is approximately 50 emu/g.)

*Most workers who responded to this questionnaire use (emu/g) for the "cgs" units of magnetic moment. To convert this to SI units, multiply by $4\pi \times 10^{4}\ \rho$, where $\rho$ is the density of the material in $g/cm^3$.

3F. Temperature (other than room)

| Temperature | Number |
|---|---|
| 4.2 K | 26 |
| 77 K | 13 |
| 4.2 K to 293 K | 4 |
| | 43 |

Approximately 35% of the workers would like an SRM to check or calibrate their equipment at low temperatures.

3G. Other Specifications (list)

Only one person responded, and the response did not pertain to magnetic moment considerations.

Question 4: If the proposed SRM (3 mm diameter nickel sphere) were available for approximately $150, would you purchase it?

Yes No

Table 17. Response to Question 4

| Classification | No | Yes | Yes, if accuracy is better than 5% (write in)** | Total Yes | Percent Total Yes (normalized) |
|---|---|---|---|---|---|
| Industry | 5 | 23 | 7 | 30 | 46 |
| University | 11 | 21 | 6 | 27 | 44 |
| Government | 4 | 6 | - | 6 | 9 |
| Private | - | 2 | - | 2 | 1 |
| Unknown | 9 | 26 | 4 | 30 | - |
| Total | 29 | 78* | 17 | 95 | |
| Percent | 23 | 63 (78/124) | 14 | 77 | |

*This includes 19 maybe's.
**Seventeen people who answered this question wrote in "Yes, if accuracy is better than 5%."

The responses to this question show that 63% of the 124 responses would buy the 5% SRM for $150 even though many prefer a more accurate SRM. Response to question 3D showed that 50% of the workers claimed they needed an SRM to better than 5%. A total of 77% (95/124) would purchase the SRM if it were certified to better than 5% accuracy. Approximately 46% of the potential customers are companies, 44% universities, and 9% government. Only 14% (17/124) would not buy an SRM with an accuracy of 5%.

Question 5. Please list the names and addresses of any persons you feel would be interested in an SRM for magnetic moment. This question brought 44 responses.

## 5.3 POSSIBLE USERS

We mention here who the users of these standard reference materials might be.

### 5.3.1 Industry

Users of vibrating sample magnetometers in industry require such standard reference materials for calibration purposes. Vibrating sample magnetometers are commercial instruments and are widely used. In fact, two SRM's with different moments have been suggested. They would be used to determine the linearity of magnetometers.

Producers and customers of rare earth cobalt magnets need such standard reference materials to certify field measurements traceable to NBS.

### 5.3.2 Universities

Researchers at universities also request SRM's for vibrating sample magnetometers. Others state a requirement for magnetization standards with moments as small as $10^{-3}$ emu/g. The latter standards interest researchers concerned with the magnetism of rocks (both terrestrial and lunar). Some investigators suggest standards to calibrate mutual inductance systems for measuring differential susceptibility at liquid helium temperatures. This latter suggestion involves a non-metallic sample. Preferably the sample should be an optically transparent, magnetic insulator with a known Faraday rotation.

### 5.3.3 Government and Others

Additional potential users mention the need to calibrate sensitive Faraday magnetometers, Faraday microbalances, torque magnetometers, and hysteresigraphs by insertion of known samples.

## 5.4 SUMMARY

The 124 responses were from workers who are active in the field of magnetism. Approximately 87% of these 124 workers use a calibrant (mainly nickel). Approximately one-half of the workers want a certified SRM. However, some workers have confused precision and accuracy. Also, none of the workers who have used a reference material volunteered to state the accuracy of their own calibrant. Some workers thought the price of $150 was too high.

There is an uncertainty in the value of saturation magnetization for nickel in the literature. Values given by reliable sources vary by about 8%. Workers do not know what value to use.

If NBS issues an SRM for magnetic moment, it should probably have the following properties:

1. Accuracy within ±1%.
2. More than one size (perhaps a 1-mm and a 3-mm sphere).
3. Material most likely of nickel.
4. A price less than $150.00.
5. The actual magnetic moment determined at known values of magnetic field (H) greater than 5000 oersteds.

### 5.5 TECHNICAL REFERENCES


(1) "Calibration of Vibrating-Sample Magnetometers," J. Res. Natl. Bur. Stand. (U.S.) C. Engineering and Instrumentation, Vol. 70C, No. 4, October-December 1966. W. E. Case and R. D. Harrington.

(2) "The Magnetization of Pure Iron and Nickel," Proc. Roy. Soc. London A321, 447-491 (1971). J. Crangle and G. M. Goodman.

(3) "New Determinations of the Saturation Magnetization of Nickel and Iron," J. Appl. Phys. 39, 2 (1968). H. Danan, A. Herr, and A. J. P. Meyer.


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This publication contains the analyses of three survey-questionnaires to assess the needs and markets for standards in Raman spectroscopy, electron paramagnetic resonance, and magnetic moment measurements. These analyses give the requirements and suggest the strategies to be followed for making each of the above three measurement methods more quantitative than they are at present. Some of the requirements are data cataloging, standards for data presentation, standard reference materials, and standard reference data.


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