

ANALYTICAL RAMAN SPECTROSCOPY IN NUCLEAR TECHNOLOGY

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ABSTRACT

Applications of laser Raman spectroscopy in the nuclear fuel cycle are briefly reviewed. These include, among others, the characterization of solids formed from fuel reprocessing solutions using the Raman micro-probe technique, measurement of low contents of TBP in PUREX solutions and determination of oxyanions in nuclear waste materials. Some areas where Raman spectroscopy can profitably be applied in nuclear technology are indicated.

INTRODUCTION

NUCLEAR energy promises to continue as a major source of energy for both developed and developing nations of the world. Since a variety of specialized services are needed for the successful operation of the nuclear power plants, the major goal of the national nuclear research laboratories has been to study the various requirements of the nuclear fuel cycle that encompasses the three major parts: the procurement and fabrication of the fuels, reprocessing of the spent nuclear fuel and the safe disposal of the wastes generated. There is, therefore, a growing interest in the chemistry of the nuclear fuel cycle covering practically all its branches¹.

One of the tasks of a radiochemist is concerned with the elemental and molecular analysis of the active samples at different stages of the cycle. A large number of instrumental methods are now available for this purpose and some of the important among them, for elemental analysis, are x-ray fluorescence, atomic absorption and emission spectroscopy, α - and γ -ray spectroscopy and mass spectrometry. However, not many techniques can be easily applied for molecular characterization of the active samples; firstly because, active samples of large size are required and secondly because, the adaptation of an instrument for radioactive work is not always

simple. One of the techniques that seems to overcome both these difficulties is laser Raman spectroscopy (LRS), thanks to the recent advent of Raman microprobe spectroscopy and the development of fibre optics for efficient Raman sampling. The other two techniques—scanning electron microscopy and electron probe microscopy—, though useful for the characterization of sizes, shapes and elemental composition of single particles, do not provide information on molecular and crystal identification.

The main purpose of this article is to give an account of the work that is currently in progress in this and other laboratories on the analytical applications of LRS in nuclear technology, a relatively new area of its application². This review is, however, limited to the spontaneous Raman scattering studies. Our work³⁻⁸ is concerned with the nature and characterization of solids formed in fuel reprocessing solutions using Raman microprobe spectroscopy, the possible use of surface enhanced Raman scattering (SERS) for the determination of low contents of tributyl phosphate (TBP) in PUREX solutions and the analysis of oxyanions in nuclear waste materials by multichannel detection besides the adaptation of the spectrometer and the development of a fibre optic Raman probe for radioactive work. These studies have been made on simulated systems but will be soon extended to real radioactive samples. Before discussing the results of our experiments, the instrumental set-up used in our laboratory is briefly described.

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RAMAN MICROPROBE SPECTROSCOPY

The first successful measurement of Raman spectrum of microparticles by Rosasco *et al*⁹ and the realisation of a Raman microscope by Delhaye *et al*¹⁰ in 1974 opened up a new line of research in Raman spectroscopy for microanalysis. Following this initial report, both the groups have developed Raman microprobes and the one developed by the latter is now commercially available as MOLE (molecular optics laser examiner). It combines a microscope to a spectrometer that can produce images as well as spectra of individual particles. During the last 10 years, a large body of experimental research has been conducted on Raman microanalysis and several reviews have appeared¹¹⁻¹⁷ on its applications in a wide range of fields.

MEASUREMENT AND EVALUATION OF THE SPECTRA

The measurements—both for macro and micro samples—are made at a 90° angle with respect to the exciting laser beam with backward coated collecting mirrors for laser and scattered light using a 12 W Ar⁺ ion laser (Spectra Physics 171) either with 488 or 514.5 nm line. A Jobin Yvon Ramanor U 1000 double monochromator with holographic gratings (1800 lines/mm) coupled with a Nacet microscope is being used for microanalysis. The sample image is displayed on a screen by a TV camera. This arrangement is schematically shown in figure 1. The microscope has both reflected and transmitted light capabilities enabling the analysis of both opaque and transparent substrates. A number of focussing objectives (4–80×) and ocular (12.5×) are available providing a maximum magnification of 1000.

The viewing system can be moved along X-Y direction and it is, thus, possible to record the spectra of the microparticles under point mode illumination. In our regular experiments, the spectra are recorded using a magnification of 200 and the sample viewing is done by reflected light. The spectra are measured using a slit width corresponding to about 5 cm⁻¹ and a laser power

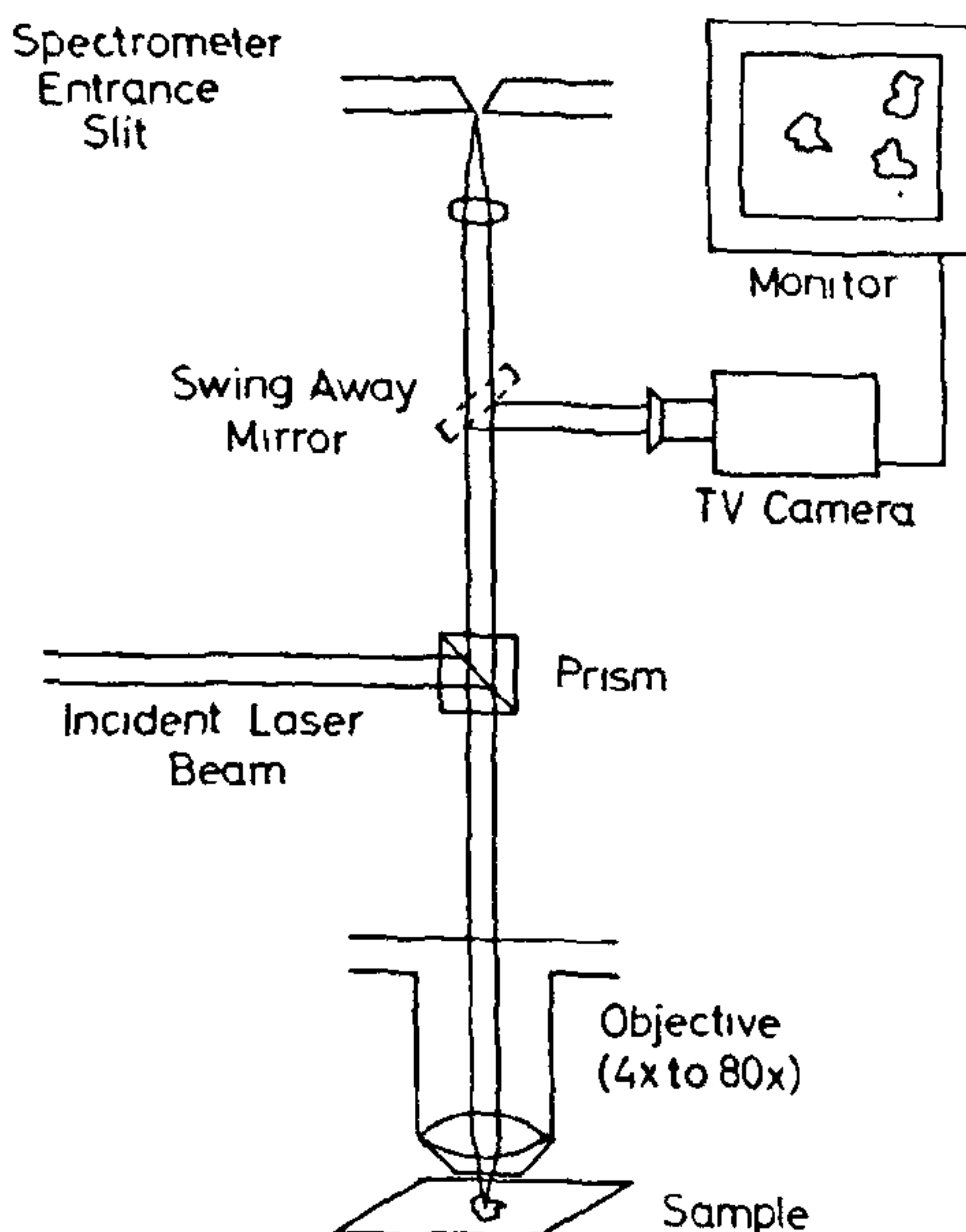


Figure 1. Schematic diagram of the experimental set-up used for the Raman microprobe spectroscopy.

of 1 W for macro and 58 mW for micro samples. The wavenumbers are spaced by 1 cm⁻¹ with an integration time of 0.2 s and the analysis, under these conditions, lasts less than 15 min.

Special cuvettes with a maximum capacity of 200 μl or melting point capillaries are prepared for future use in the analysis of radioactive samples. One of the cuvettes has a flat bottom for efficient collection of the scattered light with vertical ends for pipetting and cleaning purposes. A thick protective PVC box with glass plates on the 4 sides encloses the cuvette which can be mounted in the sample chamber (figure 2). The operation of the spectrometer, data acquisition and evaluation is performed by a Columbia computer (type 964) with a plotter and a printer as output devices. The data are evaluated by the software provided by the manufacturer. Recently, an optical simultaneous multichannel analyser (OSMA) with the accompanying computing system from Spectradata is added.

The OSMA (Spectroscopy Instruments) detector

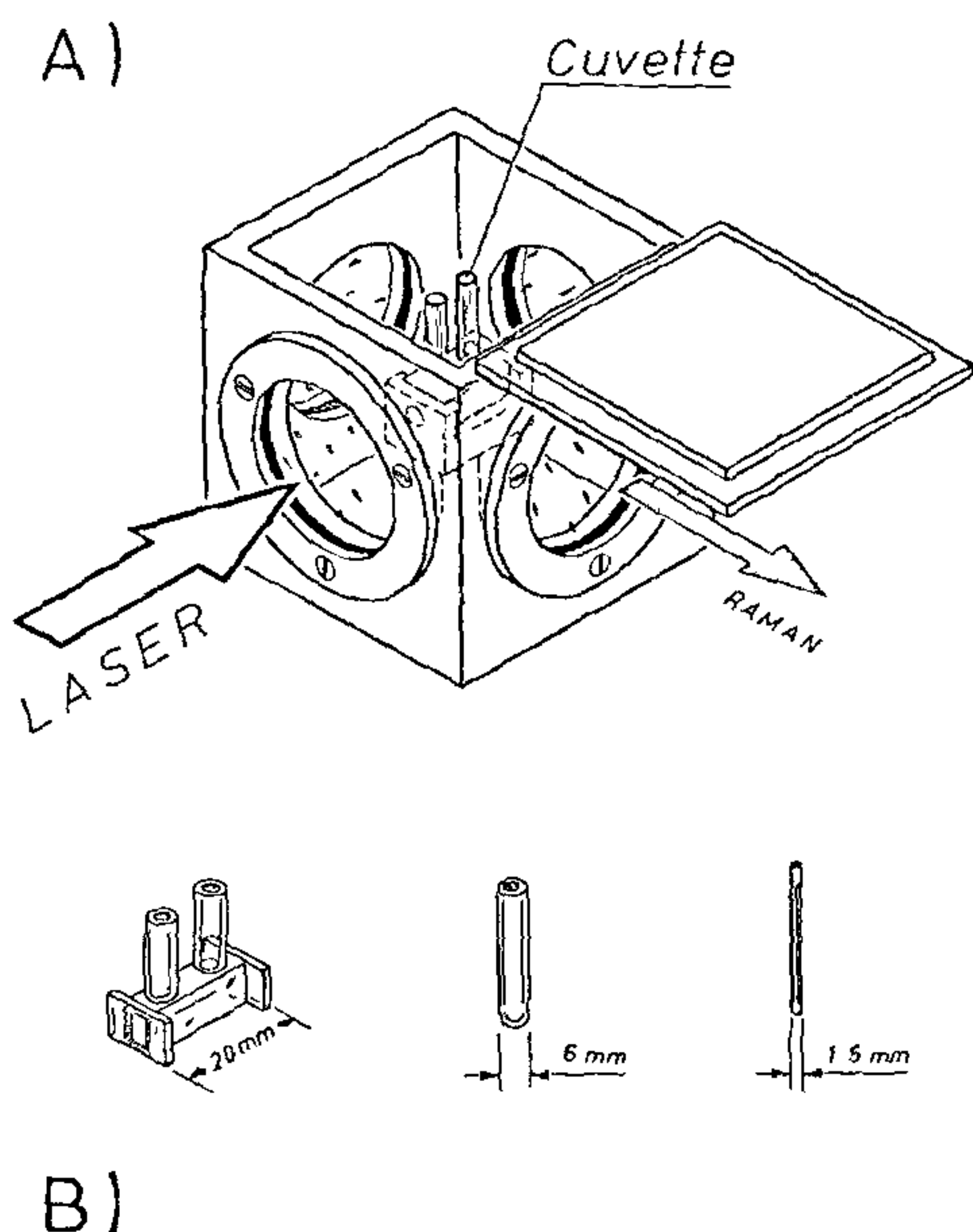


Figure 2. The protective box (A) and the cuvettes (B) prepared for the measurement of radioactive samples.

head comprises an optoelectric image device with the associated electronics necessary for its optimized manipulation. The detector controller provides power to the detector head besides temperature thermostating, signal conditioning, setting exposure time, gathering and averaging the data and transmitting them to the computer. The spectra can be either recorded simultaneously using OSMA or sequentially by the photomultiplier.

DEVELOPMENT OF A FIBRE OPTIC RAMAN PROBE

Since fibre optics transmit visible light efficiently compared to infrared, Raman spectroscopy can be advantageously used for the analysis of the samples remote from the spectrometer. Recently, a versatile and efficient fibre optic Raman probe has been developed^{18,19} in which both the exciting laser line and the scattered Raman light have been conducted by optical

fibres and it has been shown that the Raman signal, depending on the configuration of the probe was 1 to 9 times as large as that from a conventional liquid sampling device. In our laboratory, a similar light guide system is tested.

APPLICATIONS OF LRS IN NUCLEAR TECHNOLOGY

1. *Characterization of Solid Residues Formed in the Fuel Reprocessing Solutions.* Insoluble solid residues are known²⁰⁻²³ to exist following the dissolution of the spent nuclear fuel. These residues principally involve alloys of the noble metal fission products and cladding wastes—usually referred to as “hulls”—arising from hardware and undissolved fuel particles. These solid residues can be removed from dissolver solution by centrifugation or filtration. The fission product residues are spherical particles composing mainly of Mo, Tc, Ru, Rh and Pd. They along with other undissolved fuel account for nearly 60–80% of the residue.

In addition to the formation of the solids referred to above, the work^{21,24,25} at the Oak Ridge National Laboratory has shown that precipitation occurs in clarified feed solutions on extended periods of standing and/or heating. These arise from the solution instabilities and are due to the precipitation of zirconia and Zr and Pu molybdates. We have, recently, reported^{6,7} the Raman microprobe spectral studies on zirconium molybdate formed from simulated fuel reprocessing solutions under varying experimental conditions normally encountered in process operations. These studies were complemented by several other techniques for both elemental and molecular analysis.

Our data are generally in agreement with those reported by the Oak Ridge group^{21,24,25} who observed similar yield curves for the formation of hydrated zirconium molybdate. The Raman spectra of the microparticles of the hydrated form and those heated at 200°C and 550°C are shown in figure 3. The spectrum of the hydrated form exhibited several major bands: 939, 837, 722, 539, 366, 275, 255 and 155 cm^{-1} . The peaks of the spectra of the dehydrated samples (heated

at 200°C) were broad and not well resolved unlike from those of the samples heated further. The frequencies of the samples ignited at 1000°C are in accord with those reported for monoclinic ZrO_2 ^{26, 27}.

This fact was also revealed by the x-ray studies⁸ which have indicated that the hydrated form has a tetragonal structure as reported earlier²⁸ for $ZrMo_2O_7(OH)_2 \cdot 2H_2O$ and the samples heated at 550°C were indexed as having hexagonal symmetry as found before^{29, 30} for $Zr(Mo_4)_2$. However, the particles heated at 200°C have shown broad unidentified peaks with some traces of hexagonal structure in some samples.

One intriguing observation from the results of elemental analysis was that more Mo than necessary for the stoichiometry of $ZrMo_2O_7(OH)_2 \cdot 2H_2O$ was precipitated in most

cases. However, the presence of compounds other than this was not evident from the Raman spectra except in solutions with large excess of Mo (6 mg/ml). In these solutions, the spectra of some microparticles were different from those observed with hydrated zirconium molybdate; but they were similar to the spectra of some of the particles precipitated from HNO_3 solutions containing only Mo. The latter, perhaps, arise due to the precipitation of molybdic acid and molybdenum oxide. Figure 4 shows the spectra of the microparticles precipitated from these solutions, commercial molybdic acid and molybdenum oxide. It can be noted that the former spectrum is a combination of the Raman bands, with slight shift in frequencies, associated with molybdic acid and molybdenum oxide.

The Raman investigation⁸ concerning the formation of solids from HNO_3 solutions in the

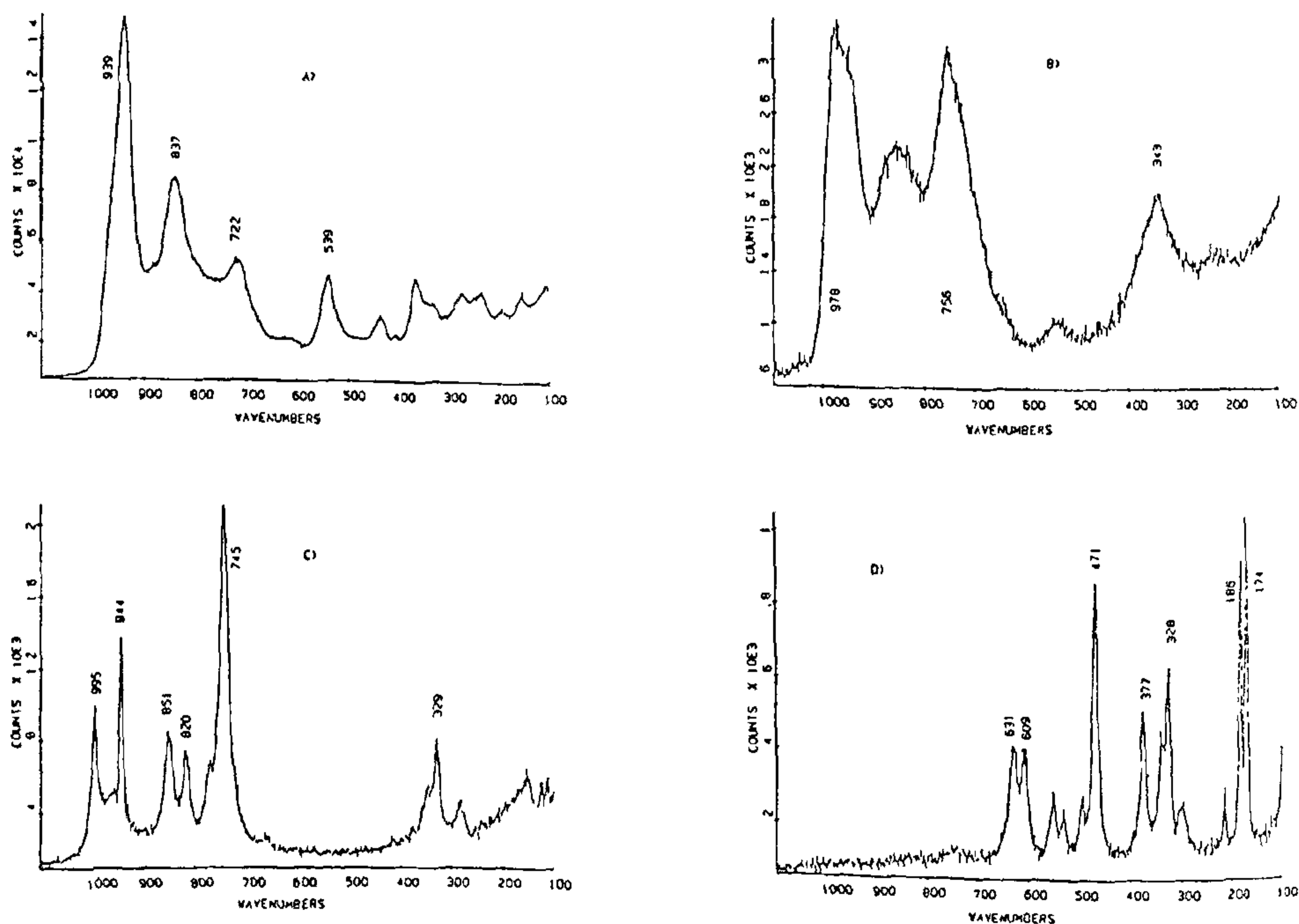


Figure 3. The Raman spectra of the microparticles of (A) hydrated zirconium molybdate and of the samples heated at (B) 200°C, (C) 550°C and (D) 1000°C. (Taken with the permission of the authors from reference 6).

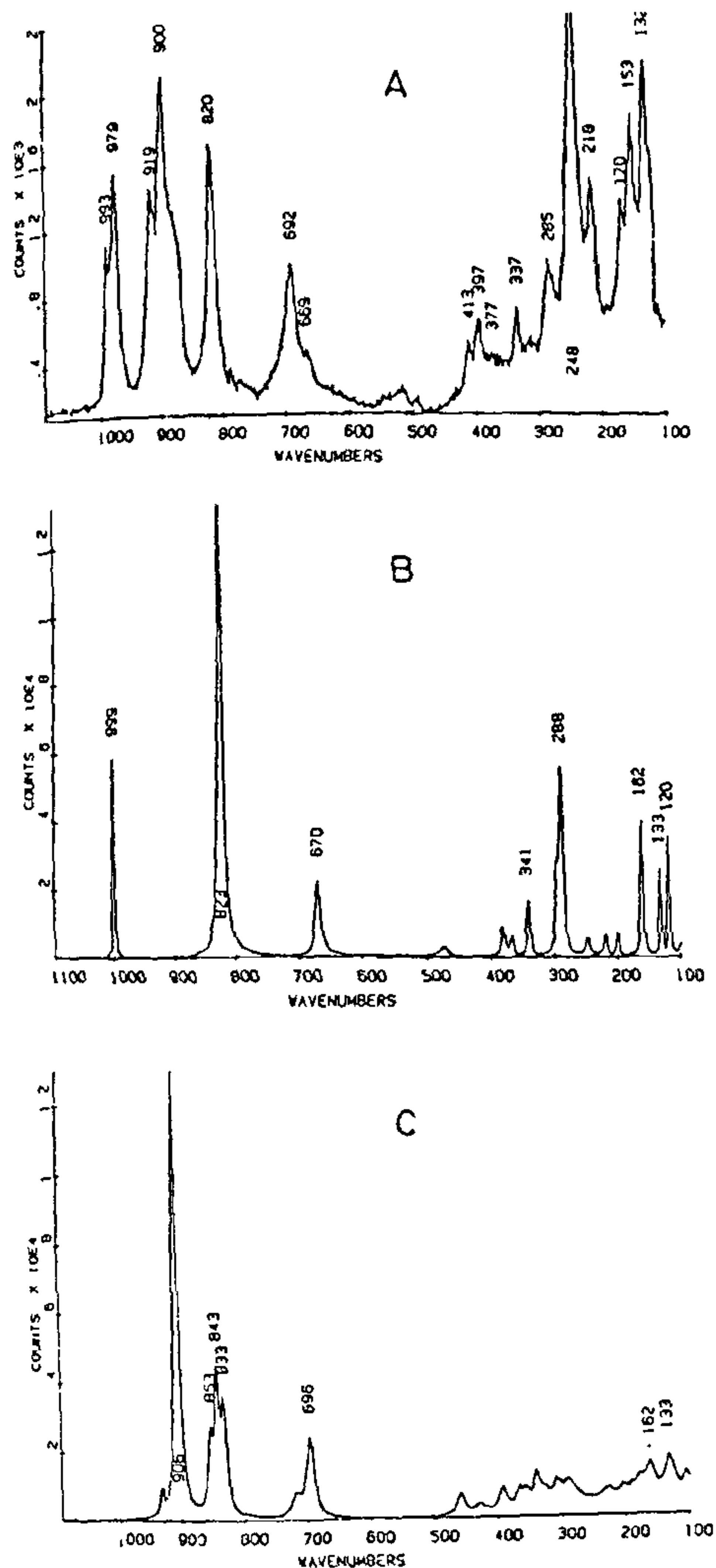


Figure 4. The Raman spectra of microparticles (A) precipitated from HNO_3 solutions containing Mo (B) molybdenum oxide and (C) commercial molybdic acid.

presence of U in addition to Zr and Mo, currently in progress in our laboratory, have indicated that hydrated zirconium molybdate was the main product formed in these solutions and only in the absence of Zr, uranyl molybdate was pre-

cipitated. The Raman spectra of this compound could not be measured using both the 488 and 514.5 nm lines due to the interference from fluorescence. However, the dehydrated form did not exhibit fluorescence and the spectra of the microparticles were in agreement with those reported by Smit and Blasse³¹ and Serezhkin *et al*³² for macroscopic samples. The latter group employed a helium-neon laser in their work and could also obtain the spectra of the hydrated uranyl molybdate using the 632.8 nm line. The difference in the spectra of the hydrated and dehydrated samples, shown in figure 5, is that the UO_2 stretches are significantly shifted to lower frequencies in the latter case.

2. Raman Microanalysis of Filter Debris Samples from a Test Reactor. Doyle and Alvarez³³ have recently reported a novel application of Raman microprobe technique in the analysis of filter debris samples from the power burst facility (PBF), a nuclear test reactor, where the fuel assemblies are subjected to high temperature accident conditions. They have utilised the titanium fluorescence as markers in the Raman spectra to differentiate between fabricated zirconia, and oxidised fuel-rod cladding. The Raman spectra of the microparticles of the

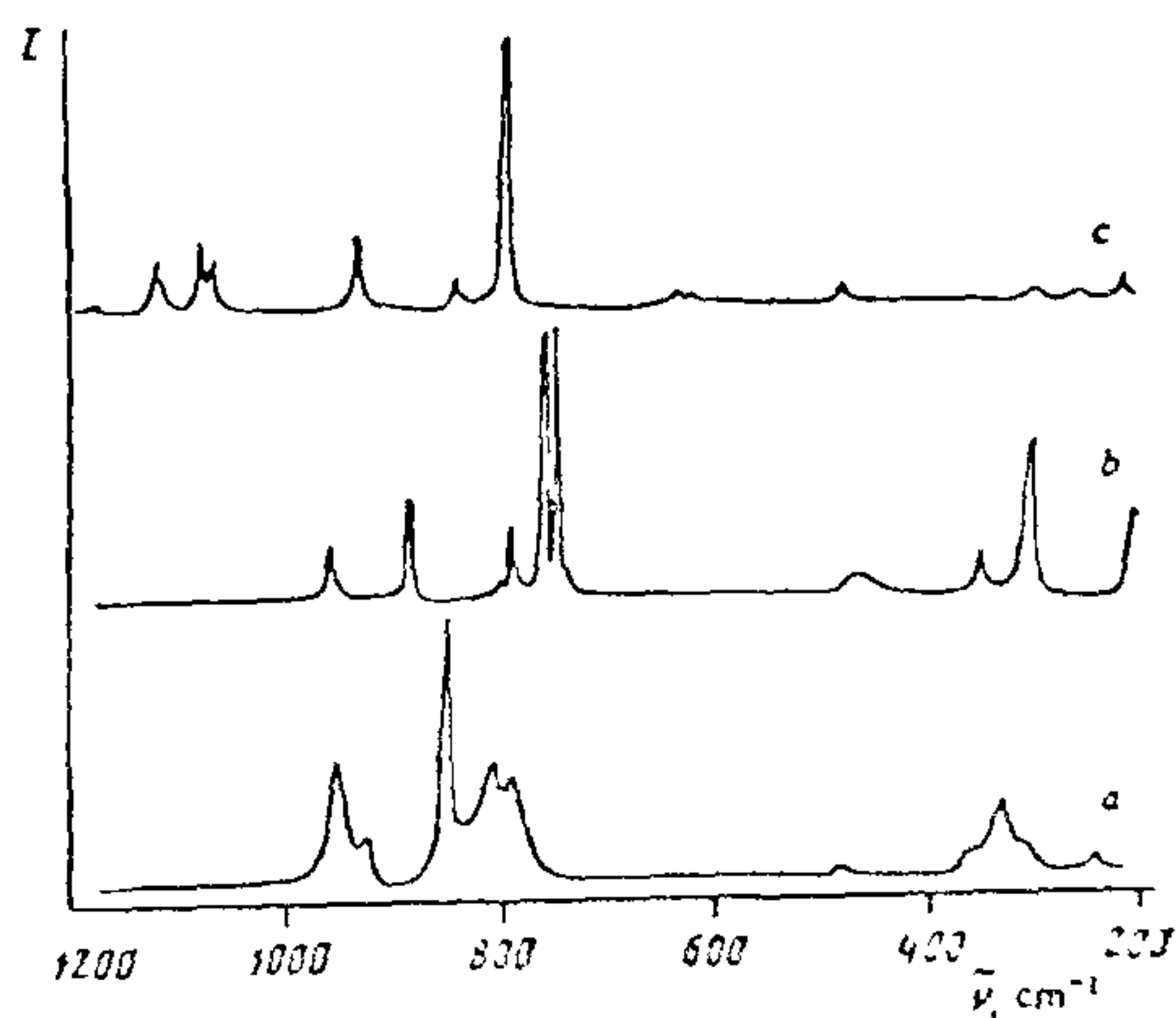


Figure 5. The Raman spectra of (a) $\alpha\text{-UO}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and (b) UO_2MoO_4 (c) $\beta\text{-UO}_2\text{SO}_4$ (taken from reference 32)

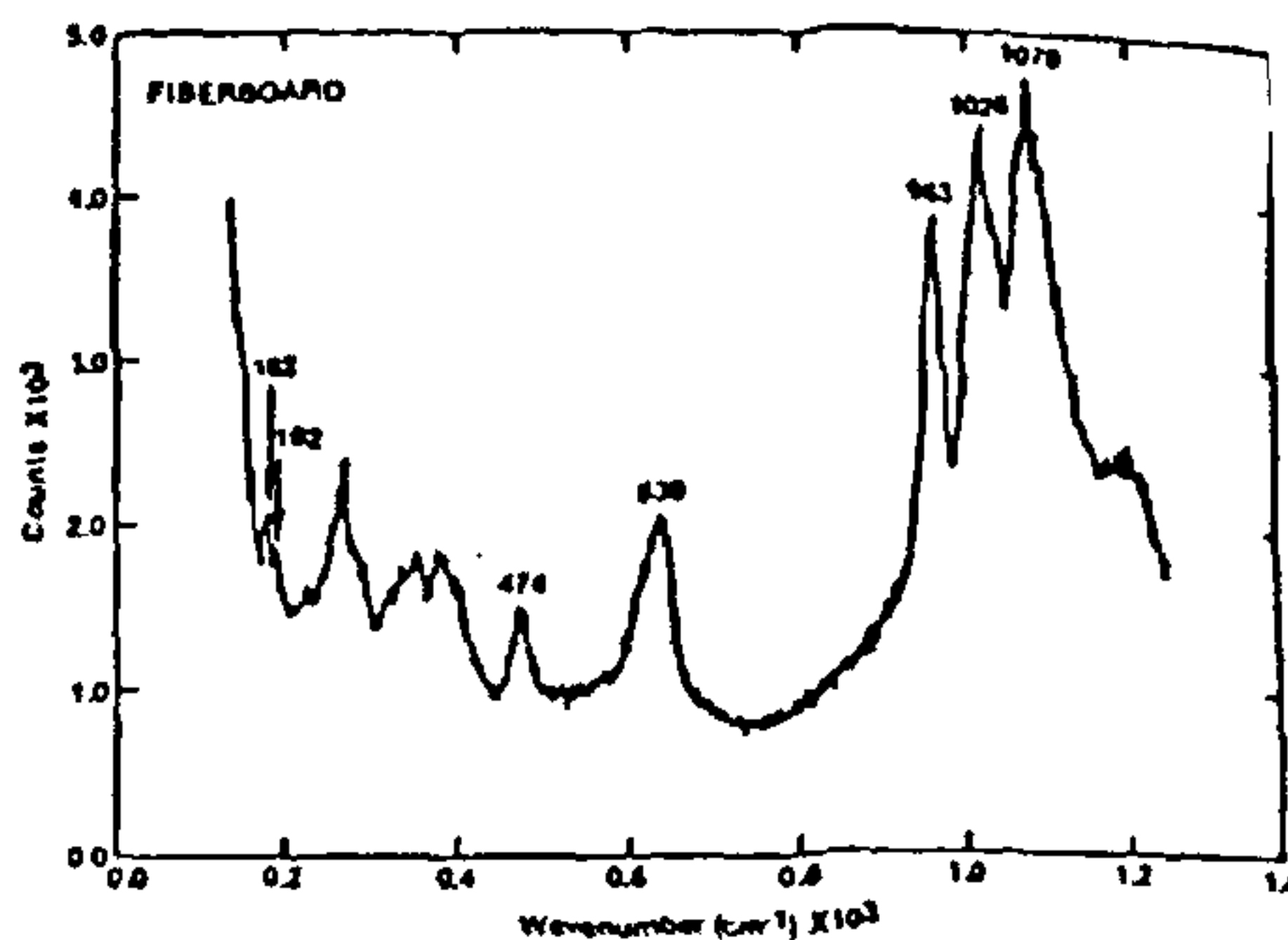
zirconia fibreboard, surrounding the PBF, have indicated the presence of both monoclinic and tetragonal ZrO_2 besides strong fluorescence peaks at 963 , 1026 and 1079 cm^{-1} due to the trace impurities of titanium (figure 6).

The PBF samples contained monoclinic, tetragonal and cubic ZrO_2 and one of the particles, identified as tetragonal ZrO_2 , produced strong fluorescence peaks suggesting its origin from the zirconia fibreboard.

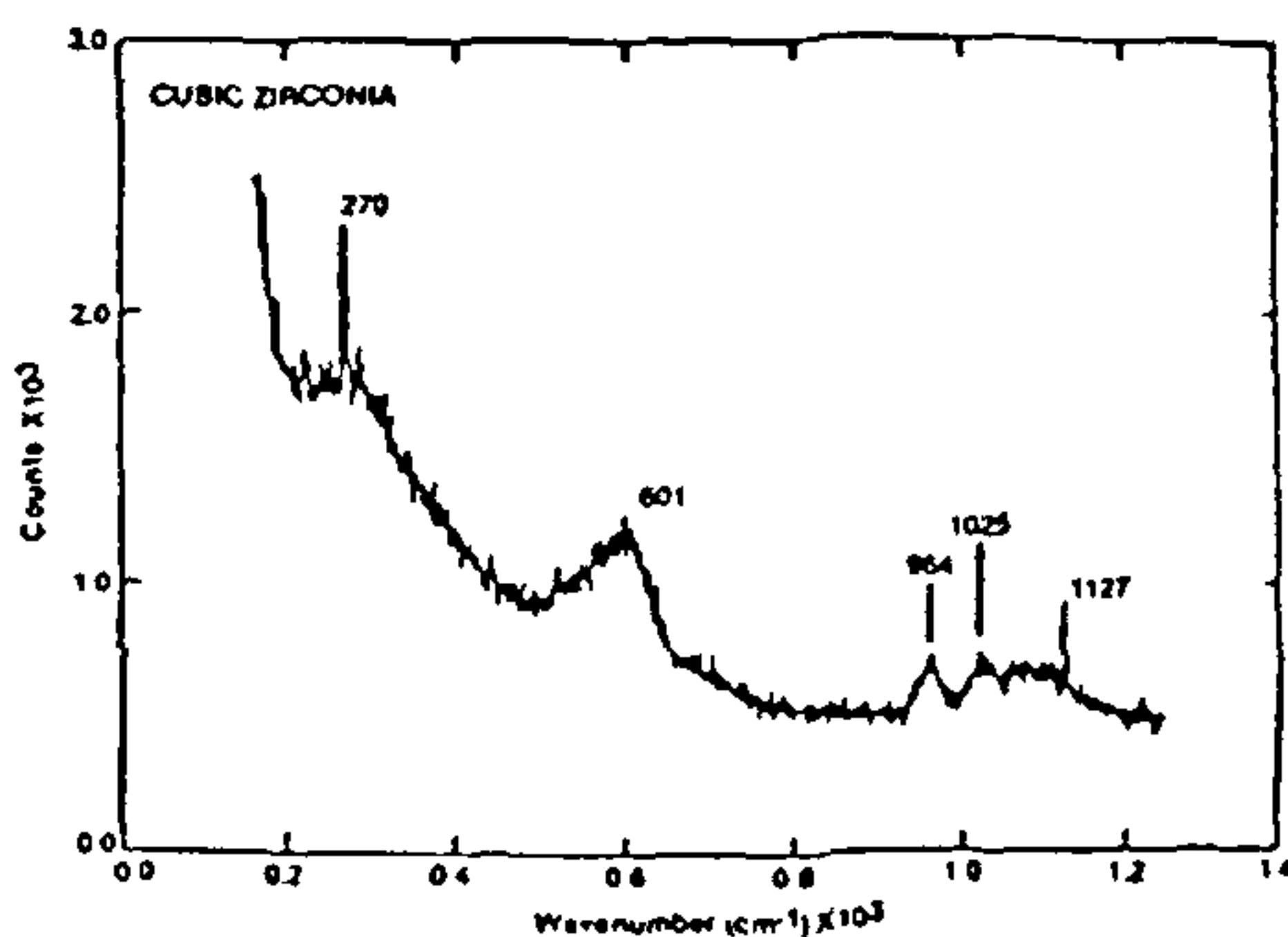
Other particles did not show fluorescence due to the absence of titanium traces and probably arose from oxidised fuel-rod cladding. These authors have suggested that the Raman microprobe spectroscopy could be advantageously employed with the use of fluorescence of lanthanides as a sensitive technique in the detection of fission products similar to radioisotope identification by γ -ray spectroscopy, though its sensitivity may not approach that of the latter.

3. *Measurement of Low TBP Contents in PUREX Solutions by SERS.* TBP, used as an extractant for U and Pu in the PUREX process, is soluble³⁴ in dilute HNO_3 solutions (10^{-3} M) to an extent of 450 mg/ml . The monitoring of its concentration in the PUREX and waste solutions is important and is normally performed³⁴ by GLC after its extraction with $CHCl_3$. We have examined⁵ the possibility for the determination of TBP in low concentrations by SERS which was reported for the first time for pyridine in electrochemically roughened silver electrodes³⁵ in 1974 and on colloidal silver and gold particles³⁶ in 1979. Several publications have appeared since then and are reviewed in refs. 37-39.

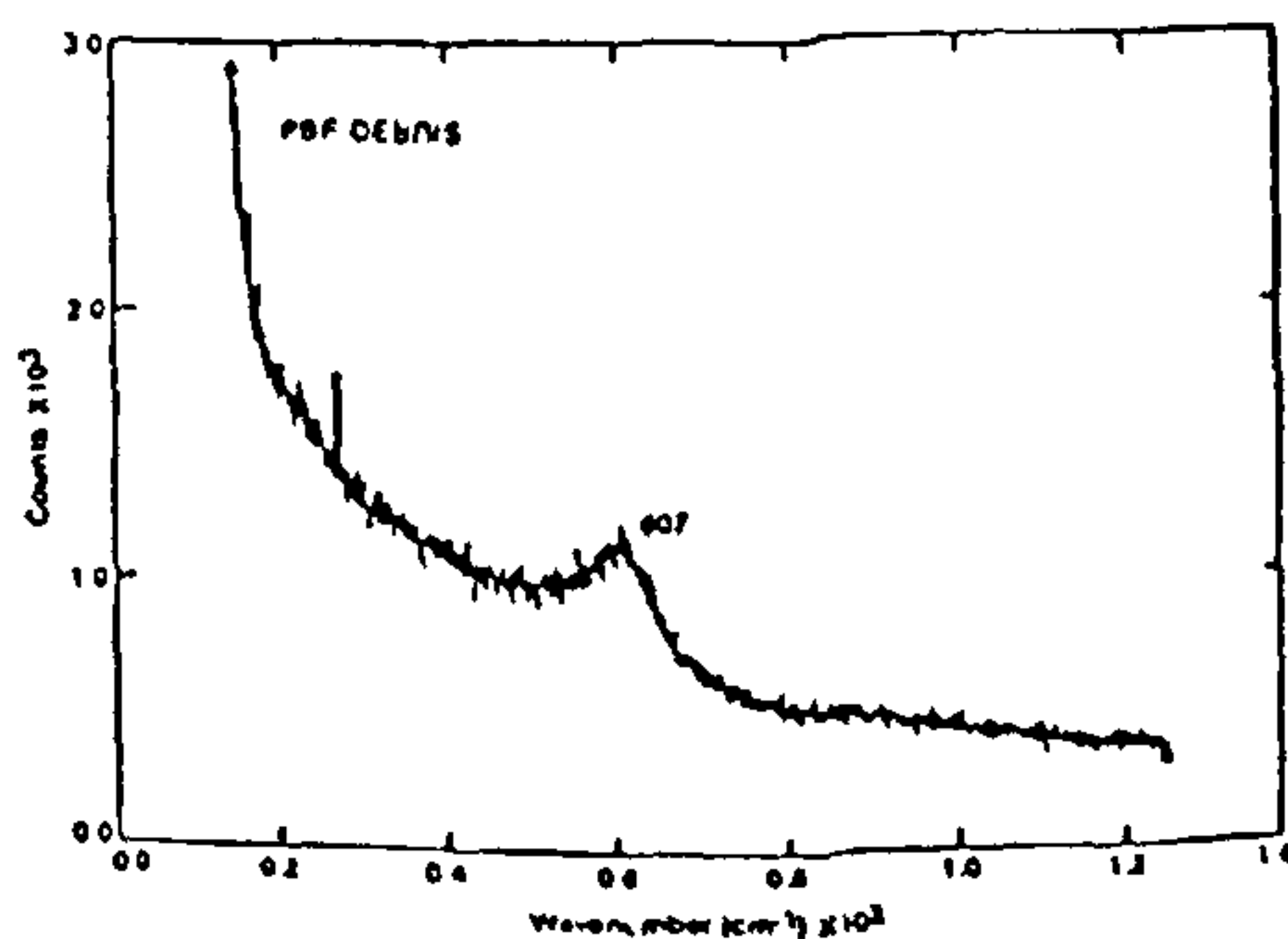
SERS studies involving metal hydrosols are simple to perform as they can conveniently be prepared and measured by simple mixing of the sol with the solution of the compound. Mixtures of TBP saturated 1 M HNO_3 with silver hydrosol yielded a Raman spectrum with bands between 600 and 1700 cm^{-1} which could possibly be attributed to SERS. This spectrum was different from that of pure TBP as can be seen from figure 7. The origin of the spectrum due to the presence of impurities and hydrolysis products of TBP was excluded by examining the mixtures of silver



-Spectrum of ZrO_2 fiberboard particle.



-Spectrum of cubic ZrO_2 gemstone.



Spectrum of cubic ZrO_2 particle from PBF debris

Figure 6. The Raman spectra of ZrO_2 particles from PBF debris (Taken from *Microbeam Analysis-1984*, p. 103. Copyright San Francisco Press Inc., by permission).

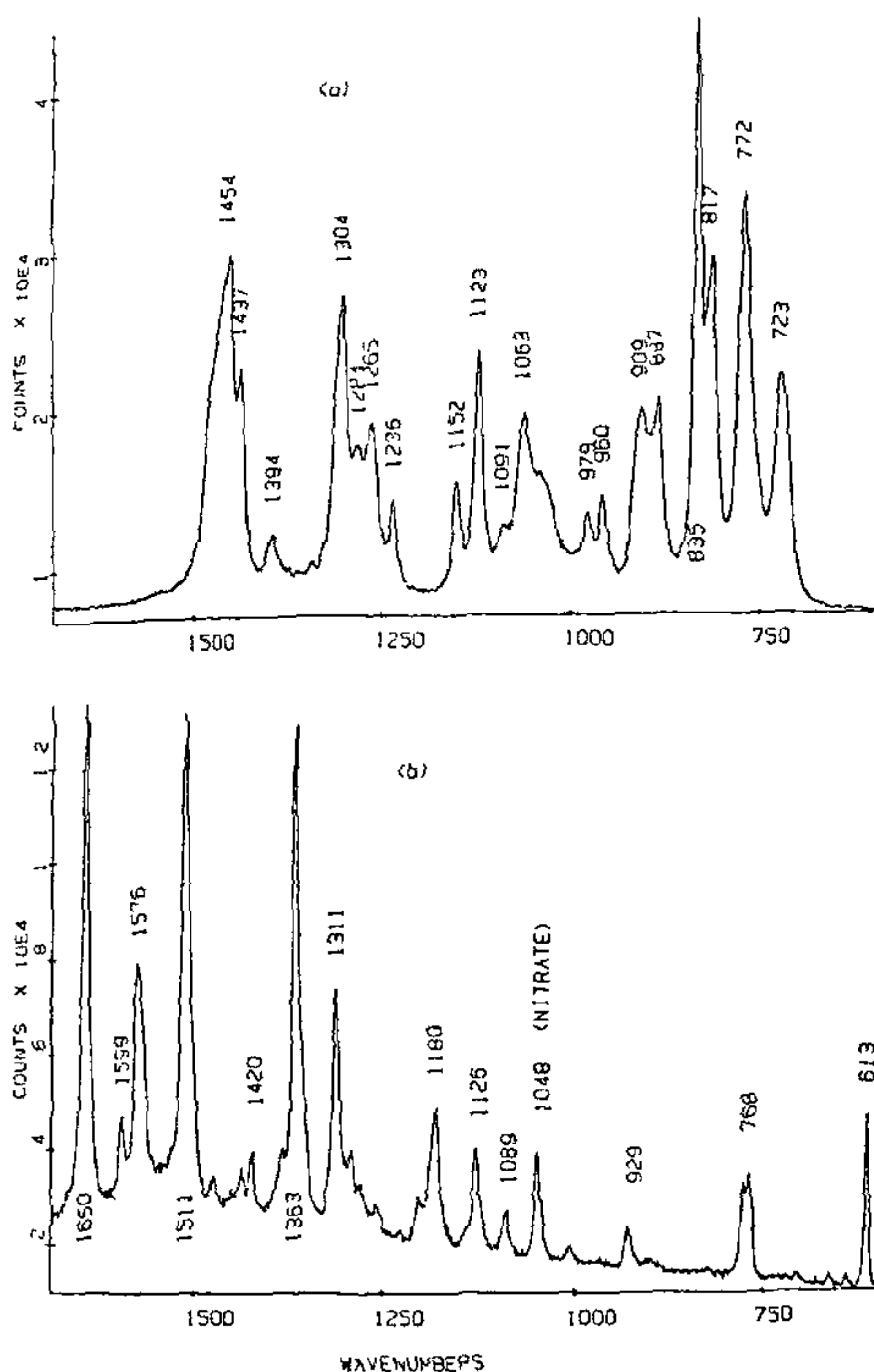


Figure 7. The Raman spectra of (a) pure TBP and (b) TBP in 1 M HNO_3 with added silver sol (Reprinted with permission from *Analytical Chemistry*, 57, 1658 (1985) Copyright (1985) American Chemical Society).

hydrosol with HNO_3 solutions containing dibutyl phosphate, 1-butanol and inorganic phosphate which constitute them⁴⁰. No Raman signal was found in these cases except the 1048 cm^{-1} band due to the nitrate ion.

Similar measurements for the detection of SERS were done with HNO_3 solutions of the homologous esters; trimethyl, triethyl and tripropyl phosphates and only with tripropyl phosphate, a similar spectrum to that of TBP was observed, though with less intensity. In the other two solutions, no bands except that of the nitrate ion were observed.

As the destruction of the hydrosol was caused by the acid with time, no Raman signal attributable to TBP was detected after 2 and 5 hr,

following the preparation of the mixture, in 1 and 0.5 M acid concentrations, respectively. This seems to be a drawback of this method for analytical purposes as the intensity was found to decrease with time even during each measurement lasting 10 min. Another limitation is with regard to the insufficient sensitivity of the method in the possible concentration range of TBP in PUREX solutions. While the former can be overcome with the help of OSMA which can drastically reduce the time of measurement, the latter needs a detailed investigation on the properties of the sols and their changes with time.

4. Determination of Oxyanions in Nuclear Waste Materials. The major species of the nuclear wastes—concentrated aqueous waste liquor, waste soluble salt cake and insoluble sludge—following the chemical processing of the spent nuclear fuel are sodium salts of oxyanions and the hydroxides of Al and Fe. Their analysis on a routine scale is important in the research and development of nuclear waste storage. Due to the complexity of the composition of the waste samples and due to the presence of many other species in trace amounts, the determination of the anion concentration in these samples is a difficult task. Martson⁴¹ and Miller⁴² have applied LRS for the analysis of the waste materials from the Savannah and Hanford plants. They have utilised the high relative sensitivity and high concentration of the nitrate ion in these samples as a secondary internal standard for the determination of the concentration of the oxyanions. Nitrate ion was determined independently by measuring the 1050 cm^{-1} NO_3^- peak relative to the 935 cm^{-1} peak of the ClO_4^- ion used as a primary internal standard. In solutions of sludges, however, standard nitrate was added as these may not contain significant amounts of nitrate. Calibration curves of 1050 cm^{-1} NO_3^- 935 cm^{-1} ClO_4^- versus $[\text{NO}_3^-]$, covering a wide concentration range, were used to determine the relative molar intensities of the anions.

Table I lists the relative molar intensities of the anions of interest reported by Martson⁴¹ and Miller⁴². LRS was found to have many advantages over other individual methods as can be seen

Table 1 Relative Molar Intensities of Oxyanions (Taken from reference 42)

Ion	Analytical line, cm^{-1}	Relative molar intensity ^a	
		Marston ⁴¹	Miller ⁴²
NO_3^-	1050	1.00	1.000
$\text{Al}(\text{OH})_4^-$	624	0.13	0.134
ClO_4^-	935		1.124
CO_3^{2-}	1070		0.913
NO_2^-	818	0.055	0.0492
NO_2^-	1330		0.125
PO_4^{3-}	939	0.16	0.182
SO_4^{2-}	985	0.95	1.030
CrO_4^{2-}	847	10.0	5.76 ^b
NO_2^-	818		0.0551 ^c
NO_2^-	1330		0.139 ^c

^a Molar intensities relative to nitrate = (ion peak height/ion molarity)/(1050 NO_3^- peak height/M NO_3^-)

^b Value based on full peak intensity.

^c Intensities measured for NO_2^- in synthetic waste liquor matrix.

from table 2 which shows a comparison of the standard recoveries and precision of this method on simple standard solutions with the results obtained by other methods. The individual methods suffer in precision when applied to real or standard simulating real samples compared to LRS except in the case of CO_3^{2-} determination by carbon analyser and PO_4^{3-} by spectrophotometry. The poor accuracy of LRS for the determination of $\text{Al}(\text{OH})_4^-$ was attributed to the high background, dimerization of the aluminate at high Al molarities (1 M Al) leading to non-linear calibration and more difficult and less accurate determination of the background due to the appearance of side bands at 540 and 690 cm^{-1} following dimerization. Other advantages of LRS is the possibility for the simultaneous determination of the anions which helps to reduce the time required for the analysis and lower levels of personnel exposure to radiation due to small sample size. It has been reported⁴² that other methods need twice as much time as LRS for the determination of the five anions even without automation and a sample size of 2 μl is sufficient for the analysis.

Table 2 Comparison of analytical results from LRS with individual methods (Taken from reference 42)

Comparison of analytical results on synthetic waste liquor

Constituent	Individual method, %	Laser
		Raman, %
1.0 M $\text{Al}(\text{OH})_4^-$	103 ± 25 (AA)	101.0 ± 11.5
0.4 M CO_3^{2-}	106 ± 21 (Grav)	
2.8 M NO_3^-	123 ± 16 (SIE)	110.3 ± 6.4
1.0 M NO_2^- (818 cm^{-1})	121 ± 39 (SIE)	104.6 ± 9.9
NO_2^- (1330 cm^{-1})		101.4 ± 7.6

Comparison of analytical results on dissolved synthetic salt cake.

Constituent	Individual method, %	Laser
		Raman, %
0.040 M Al	103 ± 25 (AA)	115 ± 15 ^a
0.075 M CO_3^{2-}	101.2 ± 2.4 (NDIR)	92 ± 8.8 ^b
0.032 M CO_3^{2-}	113 ± 13 (Grav)	
0.0018 M CrO_4^{2-}	86 ± 16 (AA)	106 ± 8.5
3.02 M NO_3^-	113 ± 22 (SIE)	109.3 ± 5.6
0.10 M NO_3^-	111 ± 45 (SIE)	117 ± 13 ^a
0.042 M PO_4^{3-}	108 ± 3.4 (Spec)	90 ± 12 ^a
0.014 M SO_4^{2-}	No method	104.8 ± 6.7

^a Concentration ~ 3x detection limit

^b Individual method involving chemical separation of CO_3^{2-} from NO_3^-

AA: atomic absorption; NDIR: Oceanography International Carbon Analyser; Grav: Gravimetry; SIE: Ion Selective Electrode; Spec: Spectrophotometry

FUTURE PROSPECTS AND CONCLUSIONS

The studies concerning the application of LRS in nuclear technology, as pointed out earlier, are limited; but there is a wide scope to expand and pursue the fundamental and quantitative aspects of this technique in this field. Some areas where LRS can profitably be applied are in the characterization of solid residues formed in the reprocessing solutions, in the analysis of U, Pu and other heavy elements in process streams and for the rapid measurement of oxyanions in the nuclear waste materials. It can also possibly be used for the measurement of TBP and the solvent degradation products. However, its use will depend on the concentration ranges and the species to be analysed due to the weak nature of the effect, the precision and accuracy of the method due to the difficulty in peak resolution, suitable standardisation methods and need for fast analysis.

LRS is based on a theory that has been well understood and instrumentation that is now well developed. The method is simple, easy to handle and non-destructive. It provides molecular information enabling simultaneous determination of a large number of species. Automated precision spectrometers with multichannel detectors are now available for accurate and rapid measurements. The possibility for the analysis of micro-particles and the development of fibre optic Raman probes makes it a valuable tool for radioactive work and should therefore, be a welcome addition to a modern radiochemistry laboratory.

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ANNOUNCEMENTS

ANNUAL CONVENTION AND SYMPOSIUM OF OIL TECHNOLOGISTS' ASSOCIATION OF INDIA

The 41st Annual Convention of the Oil Technologists' Association of India and a symposium on 'Newer technologies for augmentation and utilisation of oilseeds and derived products', will be held at the Regional Research Laboratory, Hyderabad, on **8 and 9 February 1986**. The main objectives of the symposium are to augment the production of oilseeds and to utilize them efficiently by developing newer technologies including biotechnological processes.

Original unpublished research papers are invited for the presentation. Plenary lectures will also be delivered by invited experts in these areas. A Souvenir is being brought out in this connection. The last date for registration is **31st December 1985**. For further details contact: The Honorary Secretary, Oil Technologists' Association of India, Southern Zone, Regional Research Laboratory, Hyderabad 500 007.

CONFERENCE ON LOW ENERGY ION BEAMS [LEIBMS].

The LEIB-4 conference is organised by the Atomic Collisions in Solids Group of The Institute of Physics and is co-sponsored by The American Physical Society and the Materials Research Society. The conference will be held at the University of Sussex, Brighton from **7-10 April 1986**.

The aim of the conference is to bring together

specialists in the fields of ion source development, beam transport, ion machines and the application of ion beams for the modification and analysis of solid surfaces.

For further details please contact The Meeting Officer, The Institute of Physics, 47, Belgrave Square, London SW1X 8QX.
