An Introduction to Raman Spectroscopy: Introduction and Basic Principles
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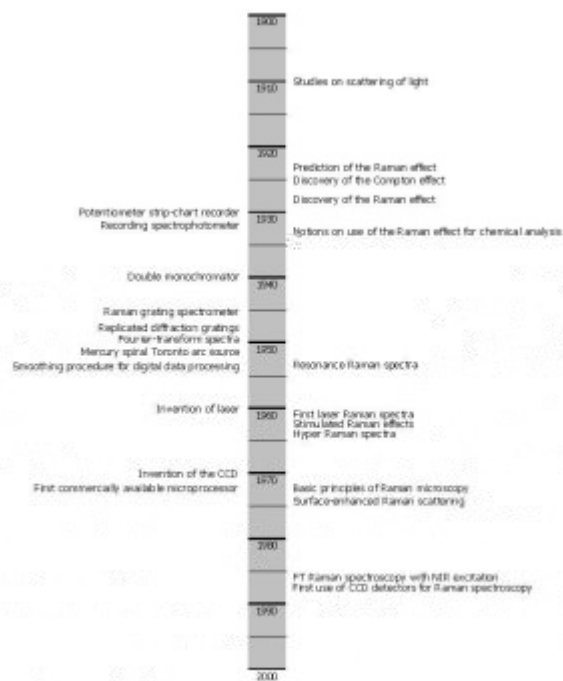http://www.spectroscopynow.com/Spy/basehtml/SpyH/1,1181,6-1-12-0-0-news_detail-0-321,00.html

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Raman spectroscopy comprises the family of spectral measurements made on molecular media based on inelastic scattering of monochromatic radiation. During this process energy is exchanged between the photon and the molecule such that the scattered photon is of higher or lower energy than the incident photon. The difference in energy is made up by a change in the rotational and vibrational energy of the molecule and gives information on its energy levels. From the beginning much of the theoretical and experimental work in Raman spectroscopy has been centered on the fundamentals of inelastic scattering and its application for understanding molecular structure. However, as the time elapsed Raman spectroscopy became increasingly important for the advancement of chemical measurements. Certainly, Raman spectroscopy has a special significance to the field of analytical chemistry as a whole, not only because of the impact of the technique itself, but also because its development anticipated a revolution in the way analytical measurements were to be made. The revolution was the insertion of powerful physical methods into a discipline that had been primarily pure chemistry.

The genesis of Raman spectroscopy was in the first quarter of the 20th century when the scattering of monochromatic radiation with change of frequency was predicted theoretically by the Austrian quantum physicist A. Smekal [1]. The scattering of light by various media had long been studied by Rayleigh in 1871, Einstein in 1910 and others, but no change of wavelength had been observed, with the sole exception of certain types of scattering in the X-ray spectral region observed by Compton [2]. With this background, many scientists were surrounding the idea of inelastic scattering, which was first reported in Calcutta by Raman and its coworker Krishnan [3] and almost simultaneously by Landsberg and Mandelstam [4] in Moscow in 1928. Two years later, Raman received the Nobel Prize in Physics for the discovery which bears its name since then.

Some historical details of the developments in Raman spectroscopy both from the theoretical and instrumental points of view are summarized in Figure 1. As with many other branches of analytical chemistry, the development of Raman spectroscopy through the years depended largely on the availability of suitable tools, and significant advances have invariably followed the invention of new instruments. This circumstance can be readily recognized by observation of Figure 1. Developments in Raman spectroscopy occurred slowly during the period from 1930 to 1950, with much of the work immediately following its discovery being devoted to fundamental studies. The rich legacy from the efforts in IR spectroscopy and the Raman work during this period resulted in formalizing a sound model of molecular vibration dynamics, setting the foundation for Raman scattering as a predictive and interpretative class of spectroscopy. Unfortunately, the basic discoveries made during this period were not followed up in chemical measurements until suitable electronic measuring devices were developed much later. When they were available advances have occurred rapidly in all aspects of Raman spectroscopy from data analysis to instrument miniaturization and, in parallel, the capabilities of Raman-based chemical measurements.

1900

1910 — Studies on scattering of light

1920
— Prediction of the Raman effect
— Discovery of the Compton effect
— Discovery of the Raman effect

Potentiometer strip-chart recorder
Recording spectrophotometer —
1930
— Notions on use of the Raman effect for chemical analysis

Double monochromator — 1940

Raman grating spectrometer
Replicated diffraction gratings
Fourier-transform spectra
Mercury spiral Toronto arc source
Smoothing procedure for digital data processing
1950
— Resonance Raman spectra

Invention of laser — 1960
First laser Raman spectra
Stimulated Raman effects
Hyper Raman spectra

Invention of the CCD
First commercially available microprocessor
1970
Basic principles of Raman microscopy
Surface-enhanced Raman scattering

1980

FT Raman spectroscopy with NIR excitation
First use of CCD detectors for Raman spectroscopy
1990

2000

Developments in instrumentation and Raman-related concepts through the 20th century. Some data associated to instrumentation had been taken from H.A. Laitinen and G.W. Ewing (Eds.), A history of analytical chemistry, American Chemical Society, Washington, 1977. Click on image to enlarge.

The experimental problems of Raman spectroscopy are the low intensity of the inelastic scattering and the much larger intensity of the Rayleigh scattering. This fact has posed several restrictions to the progress of Raman spectroscopy and had configured to a large extent the instrumentation since the beginning of the experimentation to the present. In their earliest experiments Raman and Krishnan used filtered sunlight as a radiation source and detected the Raman lines of some sixty liquids and gases. They observed the scattering light visually, using a set of compensating colored filters to enhance the optical sensitivity. A more definitive spectrum of carbon tetrachloride exhibiting both the Stokes and anti-Stokes lines recorded photographically using 435.83 nm mercury excitation was published in 1929 (5). It is interesting to note that at these early times, the Raman spectra could be obtained with relatively simpler apparatus than those required for infrared measurements. As a result at the end of the 1930s the situation was that those working on infrared group frequency analysis had often to resort to Raman data collections for reference material since the Raman spectra were more extensive and better catalogued than the corresponding infrared data (6). Nevertheless, the exposure times for photographically recording the Raman spectra were of several hours.

Early experimental work was directed toward improving the radiation sources. The mercury lamp, filtered to give essentially monochromatic radiation from one of the prominent mercury lines, became the standard source during the 1930s. Later, the mercury Toronto arc lamp became the ultimate source since its introduction in 1952 (7). However, the decisive transformation in the quality of Raman spectra came with invention of the laser in 1960 (8), which was shortly applied as a monochromatic source. In fact, in 1962 Porto and Wood (9) reported the use of a pulsed ruby laser for exciting Raman spectra. The advantages of the laser included its capabilities for focusing onto a very small sample, thus enabling excellent spectra to be obtained routinely from materials in short supply. Microgram quantities suffice since then as compared with 10^4-10^6 times these amounts in the pre laser era. Also, the laser mitigated some problems with stray light, thus improving the detection power and allowing the study of low frequency vibrations. The capabilities of

the laser to provide variable wavelength output permitted in certain circumstances to avoid the problems of fluorescence and absorption encountered with many samples. Although for many years the laser was the weaker component in terms of durability and reliability of the Raman instrument, during the 1970s most Raman instrumentation used Ar^+ lasers of appropriate stability for excitation with the lines of 488 nm and 514.5 nm. Kr^+, He-Ne, cadmium and ruby lasers were also widely employed. Following the demonstration of FT Raman spectroscopy in 1986 [(10)], the use of Nd:YAG lasers operating at 1064 nm has been generalized to decrease the fluorescence level. Optoelectronic devices have progressed dramatically in the past decade as a consequence of major achievements in solid-state technology. As a result compact, efficient, and reliable diode lasers are now available from the visible to the infrared that have been demonstrated to work properly in Raman instruments in combination with suitable filter sets.

Raman spectroscopy had always problems with the high level of elastic scattering, in particular for investigation of lines at short Raman shift. The situation has been handled by fitting the monochromator with two or three dispersion stages. The first commercially available double monochromator incorporated into a spectrophotometer was marketed by 1940 and still today double and triple monochromators are used routinely. These systems may reduce the level of Rayleigh scatter by 10 or more orders of magnitude at Raman shifts of only a few cm^{-1}. The price paid for this earnings has been an increase in the size and price of the instrument and a decrease in the throughput of the optical system. The search for alternatives has resulted in the development of high efficiency holographic notch filters for rejection of Rayleigh light, which make successive dispersion stages unnecessary thus increasing significantly the luminosity of the Raman experiment.

Although photoelectric devices were available in recording spectrophotometers by World War II, Raman detection for more than three decades was dominated by photography. Advantage was taken of the capability for light integration of photographic emulsions to mitigate the Raman detection problem. During the 1040s and 1950s much progress was made in electronics and reliable photomultipliers were developed. By 1970, high quality photomultiplier tubes were available and were universally used except for high resolution spectroscopy of gases in which photographic recording was still occasionally employed. Photocathode surfaces with efficiencies of 10-20% in the blue and green parts of the spectrum were used. In the red and near infrared quantum efficiencies were not much better than 1%. To reduce dark current, photomultiplier tubes with small area photocathodes and cooling capabilities were used. Signals were processed in pulse counting mode and digital-to-analog converted for display on chart recorders. This instrument configuration changed with the advent of array detectors. First was the photodiode array and much later the charge coupled device (CCD). In fact, although the CCD was invented in 1970 by Boyle and Smith [(11)], its use as a detector for Raman spectroscopy was first reported in 1987 [(12)]. The bidimensional capabilities of array detectors make simultaneous time-resolved signal acquisition and imaging possible. The cooling technology is now mature enough to ensure extremely long integration times with very low dark signal. Since a single reading is needed to process the signal accumulated, insignificant levels the noise from readings and from electronics are produced.

The use of computers in Raman spectroscopy occurred relatively late as compared with other techniques. This served however to gain a vast amount of technology and experience from other fields. The situation is well illustrated with Fourier transform techniques, whose evolution has been closely coupled with the development of digital computers. A primitive way of transforming the interferograms in spectra was the direct recording of the interferometer detector output in a voltmeter or ammeter, the measurement of the peak heights by hand and the completion of the necessary computation. It is clear that the mathematical process as originally devised for taking the Fourier transform was extremely long and consumed enormous amounts of time. Progress in interferometric spectroscopy was very limited as a result. Although some work was done on analog computers, the situation improved with the use of digital computers. However its generalized use only came with the development of the fast Fourier transform, a method which greatly reduces the number of required operations using the symmetry properties due to the equal steps in both the interferogram and the spectrum to achieve the transform. This method was relatively easy made compatible with the processing capabilities of the personal computers. The result was the commercial development of computer-controlled spectrometers capable of rapid acquiring, computing, and displaying high quality and resolution spectral data. When FT Raman was first demonstrated, all these technological barriers were already overcome.

Of particular significance in recent years has been the applications of fiber optics in Raman spectroscopy. Fiber optics, integrated optics and microoptics have been brought to a high degree of refinement which in combination with diode lasers expand the analytical capabilities of Raman spectroscopy. Fiber optic probes

with an ample variety of designs to satisfy the most difficult sampling demands have been described. As a result sophisticated spectroscopic measurements in traditionally inaccessible environments such as high temperature process streams and hazardous sampling locations are now possible (13).

An Introduction to Raman Spectroscopy: Current Capabilities of Raman Spectroscopy
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At the time of the Raman discovery, analytical chemistry was dealing with problems associated to the analysis of inorganic materials and analytes using wet chemistry methods. Outstanding precision and selectivity levels were achieved in many cases using a depurate technique of sample manipulation. Although the methods of analysis were discussed in terms of accuracy and representativity (anticipating the nowadays discussion of analytical properties and quality control), chemical analysis was considered primarily an instrument of trade (14). Methods of analysis were carefully chosen on the basis of speed, dependability, and cost. With this panorama, needless to say that little room existed for the use of Raman spectroscopy as an analytical tool. The low efficiency of the inelastic scattering was an added difficulty for the choice of Raman measurements as a viable analytical solution.

The first to recognize that the Raman spectrum could be a powerful resource in chemical analysis was Kohlrausch, who measured the Raman spectra of a wide range of organic compounds as early as in 1931. Later, some qualitative analysis applications were described for monitoring the progress of distillations and for detecting certain chemical groups such as nitriles, conjugated olefins, and aromatics. Soon after the Raman first grating with photoelectric detection was described in 1946 a catalog of Raman spectra of 172 pure hydrocarbons was published. From that time to the current days of powerful analytical techniques the growth of the analytical applications of Raman spectroscopy has been spectacular, with capabilities for performing conventional analytical determinations and complex measurement tasks. A wide range of measurement techniques for these purposes are available. Figure 2 shows a schematic diagram of the several faces of modern Raman spectroscopy, including its analytical uses and measurement techniques. It can be used for routine qualitative and quantitative measurements of both inorganic and organic materials, and it is successfully employed to solve complex analytical problems such as determining chemical structures. Gases, vapors, aerosols, liquids and solids can be analyzed. As well as room temperature observations, cryogenic and high temperature measurements can be made, including *in situ* identification and quantitation of combustion products in flames and plasmas. Raman spectroscopy is one of the few spectrochemical techniques amenable to both laboratory and distance measurements. Open-path optical configurations for remote sensing of atmospheric contaminants are available. Also, Raman excitation and collection using optical fibers in combination with chemical sensors have been adapted for process measurements. Raman spectroscopy can take advantage of the convenience of a range of instrumental configurations, from dispersive to interferometric systems, from monochannel to multichannel detection schemes, and a wide choice of laser systems for convenience of excitation and filter units for spectral purification.
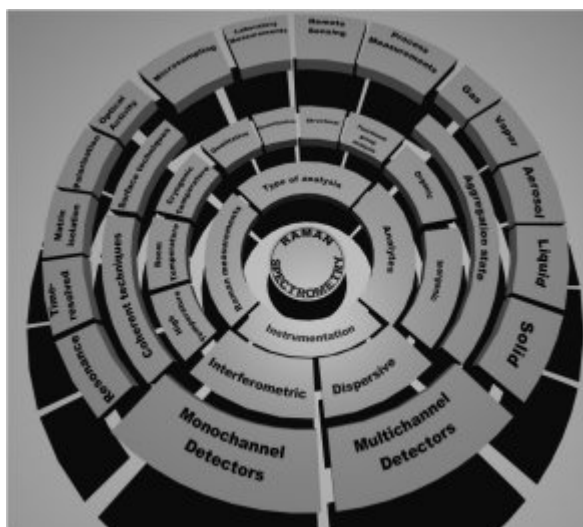
Figure 2. Schematic diagram of the current capabilities
of Raman spectroscopy. Click on image to enlarge.

A variety of experimental techniques have been developed. In 1953 the first resonance Raman spectra were reported by Shorigin, and since then the use of resonance enhancement to improve the sensitivity of Raman spectroscopy has become a very popular technique, in particular for those researchers interested in biological problems. Stimulated scattering processes based on high order dielectric susceptibility were reported for the first time in 1962 (15). Several coherent techniques have been developed, of which the most popular is coherent anti-Stokes Raman scattering which allow the acquisition of high resolution Raman spectra, not limited by the Raman spectrometer but for the linewidth of the laser line.

Micro-Raman spectroscopy has evolved rapidly from 1966 when it was pointed out that the intensity of Raman light should be independent of sample volume and should remain essentially constant with decreasing sample size down to the dimension determined by the diffraction limit, and hence the wavelength, of the laser excitation (16). With routine limits of detection in the nanogram range and high molecular selectivity, micro-Raman spectroscopy has now become a major analytical technique of application in both industry and research. Confocal optical designs and imaging capabilities have further extended the power of this approach.

The enormous enhancement of Raman intensity for molecules adsorbed on rough surfaces was first observed in 1974 (17) and then explained as a new phenomenon, the increase in Raman cross section of the adsorbed molecule by 5-6 orders of magnitude (18, 19). The name for this new technique was surface-enhanced Raman spectrometry (SERS). The interest of SERS for analytical purposes resides in its capability to provide information on molecular identity at trace concentration levels (20).

It is clear from the above that the success of Raman spectroscopy is largely due to successive improvements in experimental techniques and measurement systems, making it one of the most powerful, versatile and fascinating tools for the investigation of matter.

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