A STATISTICAL ANALYSIS OF TRENDS IN RESEARCH ON THE RAMAN EFFECT.

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In view of the tenth anniversary of the discovery of the Raman effect, it appears appropriate to make a statistical analysis of the numerous publications in this field. It is useful to determine, for example, whether the interest in this discovery has passed through a maximum—as have many other chemical and physical developments—and then waned. One method of determining this would be to plot the number of published articles on the subject or the number of manuscript pages as a function of time. An accurate determination of the number of pages is not practicable. The number of separate publications, however, can be estimated and it is found that there are nearly seventeen hundred of them over a ten-year period. The rate of publication is shown in the graph in Fig. 1.

![Graph showing the number of publications per annum on the subject of the Raman effect.](image-url)
This figure illustrates the very rapid rise in interest in the subject and the sustaining of this interest over a relatively long period. On the other hand, the graph exhibits a peculiarity which appears to be very significant and not fortuitous. This is the rather sudden drop in the publication rate which reaches a minimum in the latter part of 1933. With regard to this behaviour there are several comments which may be of interest.

The first of these is that an increase in the average length of papers might cause a diminution in the average number, but would not account for the second rise in the curve. Furthermore, a generous sampling of publication-length indicates that the average paper is about five pages in length and this has not altered greatly with time.

The possibility of the effect of the depression in the United States—which reached a maximum in 1932—on research funds, endowments and scholarships would occur to the average American. Such an effect would be a delayed one and would ostensibly account for both the diminution and the subsequent increase in the publication rate. However, a closer examination of all the pertinent facts shows that this hypothesis is, at best, only partially tenable. The over-all decrease in 1933 from the general average is 30 per cent., but in the United States where the financial situation was more acute at this particular period than abroad, it reached a value only slightly lower, namely 33 per cent., while in Germany, combined with Austria, the reduction was 47 per cent. Part of the latter reduction can undoubtedly be attributed to the known diminution in fundamental research in Germany. Finally, it can be shown that the world-wide recession in all types of chemical and physical articles in 1933 amounted to but five per cent. This seems to confirm the view that the drop in the rate of publication in 1933 on the subject of Raman spectra is significant, that it was not greatly affected by economic conditions, and that the length of articles played no obvious rôle.

These factors having been considered, the next step is to examine the possibility of a real drop in interest in the Raman effect following the fading of the first bloom of novelty. This undoubtedly enters into the picture and is probably partially responsible for the dip in the curve. However, if this is accepted as an interpretation, the re-awakening of interest after 1933 must also be explained. This becomes clear to some extent when it is remembered that the Raman effect began as a step-child of physics, but as time progressed it became the adopted son of chemistry.

It was during the period from 1932 to 1934 that the purely theoretical emphasis changed from an explanation of the origin of the Raman effect to the correlation of that effect with the modes of atomic vibration. Furthermore,
it was during this period, that there was an increased realization of the applicability of the Raman effect to structural and constitutional problems.

All the influences thus outlined may collectively play a rôle in the production rate, but as a complete explanation none of them leaves one with a feeling of consummate satisfaction. Nevertheless, these data indicate a wide and sustained interest in the Raman effect which will apparently continue for an indefinite period.

Another item of interest is the extensive distribution of research work on this subject. This may be determined from the number of publications whose experimental data or theoretical conclusions originate in various localities. This is quite distinct from nationality of the author or the place of publication. These results are shown in Fig. 2.

![Fig. 2. The geographical distribution of research on the Raman effect.](image)

This figure indicates that most of the work is being carried out in the British Empire (India, England and Canada), Germany and Austria (most of the publications of this combination originated in erstwhile Austria), the
United States, France, Italy, and the remainder in some fifteen other countries. For an individual geographical unit, India, as might be expected, is the most prolific producer of research on the Raman effect. The German-Austrian and Italian outputs differ from the others in resulting principally from the efforts of a relatively few individuals in those countries rather than from the efforts of groups of workers as in other countries.

The next items to consider from a statistical point of view are the trends indicated by the number of compounds investigated, the number of times each has been studied, and the type of compounds. From 1928 to September 1938 there have been examined 2,101 different organic compounds and 385 different inorganic substances, or a total of 2,486, discussed in 1,700 publications. The list of new compounds investigated is increasing at the rate of approximately 20 per cent. per annum taking the past three years as a criterion. Furthermore, previous investigations are being repeated. For example, it is found that the number of publications on the Raman spectra of benzene increases at the rate of 13 per cent. per annum, if the one hundred and twenty-five papers on this substance in 1935 are used as a base level.

The type of compound studied is also of interest. For the purpose of presentation these compounds are divided into two classes, organic and inorganic, and each of these, in turn, is subdivided into categories according to broad constitutional characteristics. The results obtained from the first class are shown in Table I, and are given in terms of the relation of any particular category to the largest category, namely, the halogen derivatives of aliphatic hydrocarbons. In making comparisons it should be noted that in some cases the hydrocarbons and all derivatives are lumped into one unit, while in others there is additional classification. This is done when the number in different classes would be rather insignificant.

It is noticeable from Table I that the halogen and carbonyl derivatives of saturated aliphatic hydrocarbons are more popular sources of Raman spectra than the hydrocarbons themselves. Probably this is because of the physical properties of the earlier members of the hydrocarbon series. On the other hand, the monosubstituted aromatic hydrocarbons, such as toluene, have been investigated much more frequently than any of the other derivatives. With the di- and tri-substituted compounds, however, the reverse is true and there is a diminishing popularity with increased substitution. This is easily understandable, inasmuch as the greater the complexity of the molecule the more difficult it is to allocate the Raman spectra properly, and the less clearly defined are the results.
Table I.

Relative Number and Kind of Compounds Investigated.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>Aliphatic hydrocarbons</td>
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<td>Aliphatic olefins</td>
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<td>Acetylenic hydrocarbons</td>
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<td>Halogen derivatives</td>
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<td>Halogen derivatives</td>
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<td>Halogen derivatives</td>
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<td>Alcohols and ethers</td>
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<td>Alcohols and ethers</td>
<td>9</td>
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<tr>
<td>Carbonyl derivatives</td>
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<td>Carbonyl derivatives</td>
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<td>Carbonyl derivatives</td>
<td>1</td>
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<tr>
<td>Cyano compounds</td>
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<td>Cyano compounds</td>
<td>4</td>
<td></td>
<td></td>
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<tr>
<td>Sulfur compounds</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen compounds</td>
<td>35</td>
<td>Nitrogen compounds</td>
<td>4</td>
<td></td>
<td></td>
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<tr>
<td>Metallo compounds</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclic hydrocarbons</td>
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<td>4 Polycyclic hydrocarbons</td>
<td>12</td>
<td>Heterocyclic nitrogen compounds</td>
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<td>Terpenes</td>
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<td>Heterocyclic polycyclic</td>
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<td></td>
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<td>Benzene and Mono-substituted Derivatives</td>
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<td>Heterocyclic alcohols and others</td>
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<td>Heterocyclic oxygen and nitro-</td>
<td>6</td>
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<tr>
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<td>Alkyl derivatives</td>
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<td>nitrogen or sulphur</td>
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<td>Halides</td>
<td>24</td>
<td></td>
<td>12</td>
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<tr>
<td>Carbonyl compounds</td>
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<td>Alcohols and ethers</td>
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<td>Carbonyl compounds</td>
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<td>Nitrogen compounds</td>
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<tr>
<td>Metallo compounds</td>
<td>1</td>
<td>Nitrogen compounds</td>
<td>16</td>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

* The comparison between the relative numbers of compounds is made by assigning a value of 100 to the halogen derivatives.
1 Carbonyl includes acids, aldehydes, ketones, esters, etc.
2 Includes thioethers and mercaptans.
3 Includes amines, amides, nitrates, etc.
4 Includes all derivatives not listed elsewhere.
It can be seen, therefore, that when a particular kind of compound has been examined or re-examined more frequently than others, there is usually some good reason for it. The interest in benzene has continued because it represents a characteristic class of compounds whose fundamental vibrations are not easily determined and whose symmetry is important. Carbon tetrachloride, which is equally important for the same reason, was re-examined with considerable frequency until the last three years, but now has only half the percentage increase that benzene possesses. This is because the symmetry ($T_d$) and fundamental vibrations have been determined. The continuing interest in this compound is now practically confined to the Fermi resonance effect and the influence of temperature. The number of studies on the terpenes is also out of proportion because of the interest in their chemical constitution as determined by the Raman effect. In general, the present trend with organic compounds is toward comparative determination of constitution and toward the precise determination of structural configuration through the symmetry characteristics of the molecules.

In the field of inorganic chemistry there are also preferences among the compounds studied. These are shown in Table II, which includes the principal types of compounds.

**Table II.**

<table>
<thead>
<tr>
<th>1Compounds</th>
<th>Relative No.</th>
<th>2Compounds</th>
<th>Relative No.</th>
<th>Compounds</th>
<th>Relative No.</th>
<th>Compounds</th>
<th>Relative No.</th>
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<td>Water</td>
<td>100</td>
<td>Ammonia</td>
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<td>Sulfuric acid</td>
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<td></td>
<td>82</td>
<td>Ice</td>
<td>7</td>
<td>Carbon dioxide</td>
<td>32</td>
<td>Nitric acid</td>
<td>39</td>
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<td>Carbonates</td>
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<td>Diamond</td>
<td>10</td>
<td>Hydrogen</td>
<td>23</td>
<td>Hydrochloric acid</td>
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<td></td>
<td>74</td>
<td>Silica</td>
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<td>Oxygen</td>
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<td>Carbon disulfide</td>
<td>46</td>
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<td>19</td>
<td>Perchloric acid</td>
<td>11</td>
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<td>Hydroxides</td>
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<td></td>
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<td>Phosphine</td>
<td>7</td>
<td>Orthophosphoric</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Chlorine</td>
<td>5</td>
<td>acid</td>
<td>8</td>
</tr>
</tbody>
</table>

1 Comparison made considering the nitrates as 100.
2 Comparison made for all pure compounds considering water as 100.

Of all the types of inorganic compounds examined most freely, the nitrates lead the rest. These represent the nitrates of some twenty elements headed by sodium and the ammonium ion. Ammonium nitrate has been
frequently employed because it affords a means of studying both anion and
cation simultaneously. Both nitrates and sulfates have been frequently
investigated as a corollary to experiments on the constitution of sulphuric
and nitric acids. As considerable light can be thrown on the behaviour
and structure of these acids and their derivatives by means of the Raman
effect, this accounts for the exceptional interest in acids in general and in
these two acids in particular.

The only carbonate examined frequently is calcium carbonate as calcite
or aragonite. This is because of the physical properties of the compound,
the need to determine the Raman effect as related to the symmetry of a
molecule of this type, and because of the lattice vibrations present. The
number of papers on carbon disulphide is also out of proportion in relation to
the other compounds. This may be attributed to the fact that it is a border-
line compound between organic and inorganic chemistry and because of the
splitting of frequencies in this substance due to coupling.

There is fair uniformity among the gaseous substances relative to the
frequency of investigation. This is partially because an author usually
discusses several gases at the same time. Chlorine, along with phosphine,
suffers a lack of attention for obvious manipulative reasons.

One of the most interesting features of the entire table is the demon-
stration of the remarkable interest in water. There are at present some
eighty-eight separate publications on this subject. Water has long been
known to be an abnormal substance, and it is not surprising that Raman
spectra have been frequently employed to study its behaviour under diff-
erent conditions. Water is of interest in itself because it represents the
type of molecule consisting of three atoms having a non-linear configuration;
it is the nearest known universal solvent, and it exhibits in a relatively high
degree the phenomenon of intermolecular coupling. It is this last feature
which has stimulated much of the research on water and which is demon-
strable by means of the Raman effect.

Summary.

There have been outlined in this presentation, the trends, during a ten-
year period, in interest in the Raman effect as a function of time and geogra-
phical distribution. The interest in particular types of organic and inorganic
compounds has been evaluated, and the reasons for preferential treatment
of certain classes and compounds have been discussed briefly.