# AN OUTLOOK ON ORGANIC REAGENTS IN CHINA

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Organic reagents for inorganic analysis which are among the earliest products of the organic chemical industry, exhibit a wide variety of chemical structures and are widely used. They play an important role in microdetermination, the analysis of high-purity materials and rapid analyses as well as in automatic analysis. Therefore, the study and production of various organic reagents of high quality is of great importance in the developing industry of chemical reagents.

Before liberation, most of the organic reagents used in China were imported from foreign countries, as were other analytical reagents. In the past thirty years, however, great strides have been made in the study and application of organic reagents. A reagent industry has been set up and many professionals who work at chemical analysis have been trained for the study, application and production of organic reagents. A rough analysis of the articles contributed to periodicals or journals, such as "Acta Chimica Sinica" (Huaxue Xuebao), "Chemistry" (Huaxue Tong bao), "Analytical Chemistry" (Fenxi Huaxue), "Chemical World" (Huaxue Shiji) indicates the increasing tendency for their development (See Table 1). It should be pointed out that these statistics exclude those articles published in China in some special issues e.g., industrial periodicals or university journals such as, "Acta Scientiarum Naturetium Universitatis Pekinensis," "Acta Universitatis Sun Yatseni", "Wuhan University Journal (National Science Edition)", "Journal of Lanzhou University (National Science Edition), and "Journal of Nankai University". Hence the statistics are incomplete. These articles deal with a large range of subjects

Table 1 - Statistics from Chinese Literature on Chemical Analysis and Organic Reagents

| | Number of Articles | | | Number of Articles | |
|---|---|---|---|---|---|
| Year | General Anal.Chem. | Organic Reagents | Year | General Anal.Chem. | Organic Reagents |
| 1950 | 30 | 4 | 1963 | 95 | 21 |
| 1951 | 28 | 4 | 1964 | 106 | 31 |
| 1952 | 25 | 6 | 1965 | 108 | 34 |
| 1953 | 46 | 10 | -- | -- | -- |
| 1954 | 74 | 18 | 1972 | 50 | 18 |
| 1955 | 67 | 12 | 1973 | 111 | 34 |
| 1956 | 97 | 19 | 1974 | 172 | 53 |
| 1957 | 107 | 21 | 1975 | 194 | 71 |
| 1958 | 110 | 30 | 1976 | 209 | 61 |
| 1959 | 90 | 20 | 1977 | 193 | 62 |
| 1960 | 68 | 18 | 1978 | 226 | 65 |
| 1961 | 30 | 9 | 1979 | 208 | 58 |
| 1962 | 83 | 18 | 1980 | 253 | 78 |

on presentation and synthesis of new reagents, their purification and properties, reaction principles, production techniques, theoretical studies, analysis, applications, etc.

In the last 30 years, studies of organic reagents in China have been fruitful. For example, Chinese analytical research workers have discovered and presented several new organic compounds as analytical reagents (see Table 2).

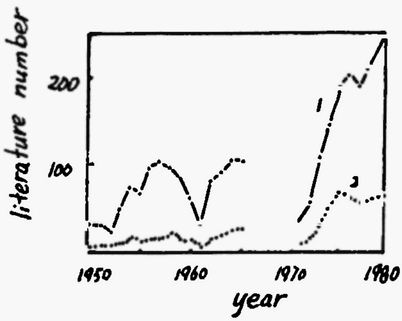
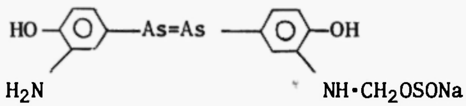



Figure: Increase in literature on general analytical chemistry and organic reagents in the P.R.C.

1. General Analytical Chemistry. 2. Organic Reagents.

Meantime, a survey of research reports on organic reagents also indicates that many papers are focused on developing new uses of organic reagents, with little attention paid to basic theories and reaction principles. In the latter sphere Wang has proposed that the -As=As- group may be considered as an analytical functional group (AFG) for silver ions. The group is involved in Neosalvarsan(I)




which was proposed as a reagent for detection of silver ions with which it forms a brown insoluble complex. The limit of identification (L.I.) and dilution limits are

Table 2 - Some Organic Compounds Used as Analytical Reagents first presented in China

| Year | Name of the Reagent | Application | Presenter | Ref. |
|---|---|---|---|---|
| 1955 | neosalvarsan | used as a silver reagent | K. Wang | (1) |
| 1957 | o-nitrobenzene sulfinic acid | used as zirconium precipitant | Q.X.Rong<br>C.J.Liu | (2) |
| 1958 | 5-aminothiazolethiocarboxylic acid-2-amide | detection and determination of palladium | K. Wang<br>P.S. Tien | (3) |
| 1962 | tetrachlorophthalic acid | separation and determination of Sc.Th | S.C. Liang<br>S.C. Hung | (4) |
| 1962 | p-iodo-amygdalic acid | precipitant for zirconium | H.X. Shen | (5) |
| 1963 | acetic ester of N-benzoyl-N-phenylhydroxylamine | precipitation from homogenerous solution for niobium | T.Z. Sun<br>Y.Jiang | (6) |
| 1964 | α-hydroxyl-a-toluene phosphoric acid | precipitant for Zr. | J.Y.Yen<br>Q.X. Rong | (7) |

Table 2 (cont)

| Year | Name of the Reagent | Application | Presenter | Ref. |
|---|---|---|---|---|
| 1964 | lactic acid | masking agent for tin(IV) titanium(IV) and antimony(V) | Y.C. Chen<br>C.Y. Hsiao | (8) |
| 1965 | glyoxal-bis(O-mercaptoanil) | detection and determination of gold | W.P. Chih<br>S.W. Zhang<br>M.C. Hsu | (9) |
| | 2-(2'-thiazolylazo)-5'-diethylaminephenol | determination for U. Sc. and V. | S.J. Hang<br>X.J. Deng | (10) |
| 1980 | mandelic acid | masking agent for Ti. | Y.Z. Chen | (11) |

found to be 2 micrograms and 25,000. Wang has studied three types of Sb reagent. They are: (1) compounds containing mercapto groups (2) Caille and Viel (cf. Compt. Rend., 1923, 176, 1156) or (cf. Anal. Abstr., 1958, 5, 458) reagents and (3) compounds containing two phenolic groups in adjacent positions. It was shown experimentally that the first two types of reagent gave reactions with very low selectivities. Moreover, the selectivity could not be improved by merely varying the structure of the reagents. The diphenolic group seems to be the most hopeful AFG for Sb ions. Compounds containing this group are quite selective. Some of them, e.g. gallein and trihydroxyaurin, were found to be satisfactory reagents for Sb ions. A detailed study has been made of the analytical reaction of some 2,6,7-trihydroxyfluorone derivatives with 73 inorganic ions by Lu and his co-workers /13/. The trihydroxyfluorones investigated include three 9-alkyl derivatives and nine 9-aryl derivatives. 9-diethylaminophenyl and 9-m-nitrophenyl-trihydroxyfluorone in alcoholic sulfuric acid solution give rise to a clear solution with antimony. 9-diethylaminophenyl-trihydroxyfluorone was sensitive to 0.02γSb/ml. When the concentration of Sb lies within 0.06-2.0γSb/ml the coloured solution formed with 9-m-nitrophenyl-trihydroxyfluorone obeys Beer's Law. Little discussion is paid to AFG because it is experimental. Recently, however,more interest has been paid to the reasons for analytical functionality according to the theories of quantum chemistry advanced by Tse and his co-workers /14/. This idea is consistent with the effort by Dilchenko /15/. In addition, little study has been made of the relationship between structure and functionality. Studies of the cyclo-structure of Calcichrome should be mentioned in this connection. Calcichrome was first synthesised and recommended as a highly-selective chromogenic reagent for calcium by Close and West /16/. Shortly afterwards, Lukin *et al.* /17/ held that the structure of this reagent was linear. Tan /18/ considered that a similar reaction of other elements which have the same radius as calcium ions should appear if Calcichrome had a cyclostructure. The position of yttrium, as a rare earth element, is just diagonal to calcium and its ion radius is the same as that of calcium:

| Atomic Number | Element | Atomic Valence | Ion Radius (A) value of determination | value of calculation a | b |
|---|---|---|---|---|---|
| 20 | Ca | 2 | 1.06 | 0.99 | 0.99 |
| 39 | Y | 3 | 1.06 | 0.93 | 0.96 |

The obvious coloured reaction between calcichrome and yttrium has been testified under the condition of pH 6.5 --10 and the composition ratio of the complex compound is 1:1. Thus the reagent is thought to have a cyclostructure.

The application of organic reagents in China has followed a pattern similar to that in other countries. Qualitative detection reagents were mainly used for inorganic analysis and precipitating agents for gravimetric analysis and precipitation separation in the 50's. For example, plasmochin (N-diethylamine-isopentyl-8-amino-6-methoxyquinolinc) was used for the detection of chromium(VI)/19/,with a limit of identification of 0.05 microgram at a dilution limit of $1:10^6$. The reagent was also used for the detection of cerium (IV), gold (III), vanadium (V) /20/, iodate and periodate /21/ etc., xylenol orange for detection of Mo(0.02 Mg and 1:1.500.000)/22/, arsenazo III for titanium (IV) (0.25 mg. and 1:200.000) /22/, p-methyl and p-methoxy thiobenzhydrazide for copper (II) (35 mg/ml. 1:28,600) /24/ etc. Chinese analytical chemists generally pay much attention to detection reagents, associated with the courses on analytical chemistry arranged in every college and university and qualitative analysis is always an important part in those courses. Secondly, precipitating agents are not widely applied, but some are very interesting, such as 4-amino-4'-chlorodiphenyl, since this reagent can be used as a precipitant for tungsten(VI) and molybdenum (VI). Studies of analytical methods for tungsten and copper are exceptionally significant because they constitute rich resources in China.

Liang /25/ first used a pH of 1.5-3.1 and found that the amounts of tungsten that could be determined by this method were 4-75 mg. Deposits of scandium and rare earth elements are very rich in China, but there are few selective and quantitative precipitants for scandium and the effective separation of scandium from thorium is difficult to achieve because their properties are so similar. Liang /26/ has presented the use of m-nitrobenzoic acid for the separation and determination of scandium and thorium. This reagent is a good precipitant for scandium because of its easy preparation, thermal stability and ability to separate scandium and thorium from the rare earths. Quinaldinic acid

/27/ and tetrachlorophthalic acid /28/ have also been used as precipitants for scandium.

In other countries, N-benzoyl-N-phenylhydroxylamine has been produced as an extractant for microgram quantities of V, Nb, Ti, La, U, Th, etc. Nee first used the reagent for extraction of tungsten (VI) in strong acid solution /29/ and for zirconium /30/. The complex of niobium with N-benzoyl-N-phenylhydroxylamine was precipitated in a coarse crystalline form from homogeneous solution by hydrolysis of the acetic ester of N-benzoyl-N-phenylhydroxylamine in an aqueous ethanolic tartrate solution at 65-70°C /31/. The acetic ester of N-benzoyl-N-phenylhydroxylamine was synthesized by mixing a pyridine solution of N-benzoyl-N-phenylhydroxylamine and acetic anhydride at 0°C. The ester melts at 57.5-58.5°C after recrystallization from ethanol.

Alimarin and his co-workers /32/ have presented and used organic derivatives of sulphurous, selenous and tellurous acid, such as benzenesulphinic, benzene-selenous and naphthaleneselenous acid forming insoluble salts with Nb, Ti, W, Th, Ce(IV), Hf, Sn(IV), Pb, Bi, Fe, etc. On this basis, o-nitrobenzene sulphinic acid was recommended as a zirconium precipitant by Rong /2/, O-nitrobenzene sulphinic acid surpasses its mother compound benzene sulphinic acid in reaction selectivity. Under the above-mentioned conditions, quadrivalent titanium and tin which form precipitates with benzene sulphinic acid are not precipitated by the orthonitro compound. The increase in selectivity is attributed to a steric effect. The corresponding paranitro derivative behaves like benzene sulphinic acid itself. Small amounts of titanium and tin do not interfere in the determination of Zr. Good results have also been obtained for the direct determination of Zr in the presence of Fe, U, Al, Ce, Mn, etc.

From the 60's to the 70's the emphasis in work on organic reagents shifted to chelating titrimetric and spectrophotometric analysis. Titrants, indicators and masking agents were accordingly studied and applied. In the first place the study and application of masking agents in complexometric titration are the main subject of many articles. For example, lactic acid is a good masking agent for titanium(IV) in acidic media according to Chen and Li /33/. At pH 5.3 and 5.8, 10 ml of 1:4 ($^{v}$/v) lactic acid masks up to 70 and 40 mg of titanium respectively. Ions such as Fe, Al, Pb, etc., which are not masked by lactic acid can be titrated without interference from titanium. Lactic acid has also been found to be a good masking agent for tin(IV), titanium(IV) and antimony(V) in EDTA titrations. Consequently, the selectivity of tin titration is enhanced greatly. With this method, tin in tin-base or lead-base alloys can be determined accurately and rapidly /8/. Culp /34/ made the basic determination of titanium and aluminium in binary alloys via EDTA titrations with lactic acid as the masking agent for titanium as presented by Chen. Because titanium-aluminium binary alloys are widely applied in the aircraft turbine industry, rapid and simple analysis there is of great interest to analytical chemists. Chen also found that at pH 5.6 malic acid has a much more powerful masking action towards the light rare earth elements than lactic acid. It was found that only malic acid can displace EDTA from RE-EDTA complexes quantitatively. In this way, 40-1,000 micrograms of Ce(III) or 50-500 micrograms of mixed light rare earth elements can be so titrated.

Spectrophotometry has made considerable progress in China since the 60's, involving all types of analytical procedure and instrumentation both in depth and width. This method which is usually based on colour complex formation is now a well-established and universally employed technique for simple, rapid and -- above all -- inexpensive determination of a large number of major, minor and trace elements in a variety of materials, including those which are of importance to geology, mining and metallurgy. In foreign countries the analysis of the above-mentioned are mainly made by atomic-absorption spectrometry and other instrumental methods. In China, owing to the scattered factories and mining enterprises, and consequently the unpopularity of more sophisticated analytical apparatus, the superiority of organic reagents prevails. For example, trace Mg in aluminium alloys is always determined by atomic absorption in other countries, but Chinese chemists select the simple and effective spectrophotometric method with chlorophosphonazo I as the colour reagent /35/. Rough statistics show that there are more than 100 organic colour reagents used in all trades and professions. The most used are pyridine azo compounds, diaryl azo compounds, triphenylmethane and basic dye-stuffs as well as mixed ligand complexes, ion-assoxiation complexes, micelle complexes. It must be pointed out that the study and application of complexes in analytical chemistry has been undertaken most vigorously since the 60's. Tse /36,37/, Hao /38, 39/ and Yu /40/ are the forerunners in this field. The first academic symposium on the theory of ternary complexes was held in October 1981 in Hangzhow.

The study of the preparation and application of chelating resins used as reagents for separation and concentration is of great current interest and its sphere of study /41-43/ is being continuously enlarged. More and more theory of organic reagents is being studied.. The author /44/ has introduced the method of calculating the optium acidity of solution for the reaction of organic reagents with metallic ions, and He /45/ has approached the possibility of studying the absorption spectrum of ternary complexes whilst Shi and his colleagues /46/ have introduced the computer study of formation constants (by use of a type DS-6 electronic computer) of mixed ligand complexes by spectrophotometric methods. However, the design and synthesis of reagents, sifting of a variety of reagents, study of purity, etc. are not dealt with in this paper. Happily, the Chinese Society of Chemical Reagents was established in autumn 1979 and it convenes an annual symposium every autumn (in Yantai 1979; in Shanghai 1980). The periodical "Chemical Reagents" resumed its publication in 1979. It is expected that work on organic reagents will develop quickly with deepening studies and the development of international academic exchange.

It is interesting to discuss how to accelerate the development of organic reagents. Generally speaking, an organic reagent undergoes four stages from presentation to application.

1. Design and Presentation: Before the establishment of theory, many organic reagents of quality were either natural compounds or chemical products used for other purposes, so that chance played a considerable part initially in the use of those reagents. The possibility of designing and synthesizing new reagents in accordance with their constituents and structures relies on the gradual establishment of theoretical considerations.

2. Confirmation of Structure of Reagents: Study of their Properties and Reaction Principles: Through this stage it is possible to have a better understand of the properties of reagents and to lay a foundation for their further development.

3. Industrial Production of Reagents: The development of reagent synthesis from laboratory work to industrial production is only obtained through the resolution of a succession of technical problems such as the synthetic line, production cost, product quality, etc. Only when these problems of production are solved, can a reagent be widely used in practice.

4. Application and Popularization: No organic reagent is perfect from its presentation through to its wide application in practice, it tends towards acceptance only after a long period of laborious work by many analytical chemists.

It is obvious from the above discussion that the development of organic reagents like other fields of science, is the result of social and collective cooperation. It is impossible to reach the present level if efforts are made only by a minority of individuals, colleges, research institutes and production units. Our plan for the next few years on research in organic reagents is as follows:

(1) Study the effects of constituents and structural changes of organic reagents on their analytical properties.
(2) Study basic theories of organic reagents.
(3) Make approaches to their optimum applicable conditions.
(4) Look for new routes for their synthesis and application.

In order to make much progress in all the above respects and to deepen the theoretical understanding of analytical chemists towards organic reagents, we must promote the introduction of basic knowledge and the theory of organic reagents. We must also strengthen mutual ties among users, research workers, and producers, discover more types of reagent, and enhance the quality of products. Moreover, much attention ought to be paid to popularization of basic synthetic techniques of organic reagents to reduce reliance of research workers upon the producers. In addition, academic exchanges, timely enlargement and application of research achievements are needed.

ACKNOWLEDGEMENT

The author of this paper is particularly thankful to T.S. West, Director of the Macaulay Institute for Soil Research in Aberdeen and to his own colleague F.L. Tang for their guidance and cooperation. In addition, he expresses his gratitude to his friend J. Liu for his help in translation.

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