

THE ANALYTICAL INSTRUMENTS OF THE PEOPLE'S  
REPUBLIC OF CHINA --- A REVIEW OF PRODUCTS,  
TECHNOLOGY AND DEVELOPMENT OF ANALYTICAL  
INSTRUMENTS OF THE PRC IN THE PAST THREE DECADES

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## SUMMARY

The development of analytical instrumentation in the PRC in the past three decades, the contemporary classification of analytical instruments, the main products and technologies of each category of analytical instrument and analytical instruments for pollution monitoring are reviewed.

## INTRODUCTION

Analytical instrumentation has developed rapidly in the PRC during the past three decades. The purpose of this paper is to give a general picture of the industry, products and technologies of the analytical instruments of the PRC. The history of development of the industry and the contemporary classification of analytical instrument products will also be described briefly.

## THE BIRTH AND DEVELOPMENT OF ANALYTICAL INSTRUMENT PRODUCTS IN PRC

A few small plants producing analytical instruments appeared in Shanghai in 1952, but there was no analytical instrumentation produced in China before that year. The names of the plants were Hujiang, Chuangzhao and Leitzu. They were the predecessors of the Shanghai Analytical Instrument Plant (SAIP) and the Shanghai Second Analytical Plant (SSAIP). The products produced at the beginning were a few types of simple analytical instruments for laboratory use, such as pH meters, conductometers and

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photocolorimeters. The productive capacity and technology at that time were extremely low and deficient, thus it could by no means be considered as an analytical instrument manufacturing industry. Therefore, the period up to 1957 can only be regarded as a prelude to the history of development of analytical instruments in the PRC.

The rapid development of process industries, especially for chemical fertilizers and oil refining and the petrochemical industries, which developed a little later, put forward great demands on automatic and continuous process analyzers. With the development of the metallurgical (particularly iron and steel) industry, geological prospecting and scientific researches, various types of laboratory analytical instrument and automatic or semi-automatic chemical analysis instrument were badly needed. The development of electric and electronic meter manufacturing industries provided the preliminary material basis for developing and producing these analytical instruments, so several types of process analyzers and a number of new types of laboratory analytical instrument began to be manufactured in batches during this period. Up to 1965, there were about 20 plants established mainly for manufacturing analytical instruments, the biggest among which were SAIP, SSAIP, the Nanking Analytical Instrument Plant (NAIP) established in 1958, and the Beijing Analytical Instrument Plant (BAIP) which was the largest in this field of industry and was built in 1962. Meanwhile, the Beijing Analytical Instrument Institute (BAII) was founded and charged with responsibility for general service for the analytical instrument industry

such as, standardization of the products and their main parts, long-term and short-term planning of the development of the whole trade, product testing and investigation, organizing technical exchanges and technical information services as well as research on important products and the key sensing elements of analytical instrumentation.

The analyzers produced in this period include process pH meters, conductometers, salimeters,  $H_2SO_4$  analyzers, electric conductivity gas analyzers, thermo-conductivity gas analyzers, thermo-magnetic oxygen analyzers, thermo-chemical gas analyzers, non-dispersive infrared gas analyzers, process colorimeters for liquids and gases, process gas chromatographs (prototypes) and dry-and-wet bulb hygrometers, etc. As for laboratory analytical instruments, the list of products manufactured includes automatic potentiometric titrators, pen-recording polarographs, square wave polarographs, UV and visible spectrophotometers, gas chromatographs, magnetic type mass spectrometers and mass spectrometric leak detectors in addition to pH meters, conductometers, photo-electric colorimeters, etc. There were many research achievements in designing and manufacturing quadrupole mass filters, cyclotron resonance mass spectrometers, radio-frequency mass spectrometers, x-ray microprobe analyzers, high-speed automatic analyzers for three elements in iron and steel, 60 MHz high resolution nuclear magnetic resonance spectrometers and electron paramagnetic resonance spectrometers, etc. Analytical instrument production in the PRC expanded rapidly during that period. This is the period which laid a firm foundation for the future development of analytical ins-

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truments in the PRC, and it is characterized by its sudden emergence and rapid growth and development. This in itself showed that the academic and technical personnel of the PRC had extensive contacts and were familiar with the various kinds of analytical technology, which fulfilled the primary material requirements for further development and production to catch up with the advanced world levels of technology in analytical instrumentation. The basic characteristics of the analytical instruments manufactured in that period in general were:

1. The design of most products was based on similar foreign products, especially those of the USSR.
2. Electro-chemical types prevailed among those produced in batches. The technical specifications of most of these products were at a relatively low level.
3. A rather large development of process analyzers was achieved, but in general, the stability of these analyzers was not satisfactory and in addition, due to a deficiency of necessary pre-treatment devices and users' knowledge of maintenance and service, all the practical benefits that might have been obtained from these instruments were not fully realized. Typical examples were non-dispersive infrared gas analyzers and process GC: a lot of these instruments were installed, but nearly none of them ran as well as was expected.
4. They were limited by the state of art of scientific and industrial technologies of the PRC at that time. Many electric, electronic and mechanical components and materials had to be imported, such as several models of elec-

tronic tubes, photo-tubes, photomultipliers, and various kinds of plastics and alloys (e.g. tungsten wire, Pt-Ir wire and ultra-thin Al foil), even the glass plates for making colored filters and sample cuvettes had to be imported.

5. The quality of some home-made components and materials was not good enough or could not meet the special requirements of analytical instruments, and the processing procedures were not correctly stipulated or strictly observed in many plants as influenced by the proneness to boasting and exaggeration prevailing in the PRC during a certain period of time, which seriously effected the quality of analytical instrument products.

6. Lack of reference standards for concentrations of chemical components, particularly the concentration of gas components and humidity. A deficiency of necessary calibrating devices rendered the measured results of some types of analytical instrument undependable, and had a harmful effect on the users' confidence and interest in PRC-produced analytical instruments.

The speed of development of the analytical instrument industry in the PRC fell sharply for a relatively long period after 1966 as a result of political upheaval. There was a recovery once more around 1972, and it regained a relatively high rate of development after 1976. The need for environmental protection devices greatly promoted the development of many high-sensitivity analytical instruments. Up to the present time there are about 40 plants making mainly analytical instruments,

their products being distributed over all the categories of the Contemporary Classification of Analytical Instrument Products (which will be discussed in the next section of this paper). These include ion activity meters with various kinds of ion-selective electrodes, double-beam atomic absorption spectrometers, direct reading spectrometers, laser Raman spectrometers, multi-channel x-ray spectrometers, high pressure liquid chromatographs, combined gas chromatograph/mass spectrometer/computer systems, high resolution nuclear magnetic resonance spectrometers and air and river-pollution monitoring systems equipped with complete sets of analyzers including automatic detecting and data processing facilities. In addition, many other types of analytical instrument have been made as the results of scientific research or as prototypes before batch production, for instance, a scanning high-energy electron diffractometer, a monopole mass spectrometer, a 100 MHz pulse Fourier transform NMR and a 250 MHz NMR. These products and the achievements of scientific researches characterize the scientific and technological achievements of the PRC in making analytical instruments, some of them approaching the performance of those in the advanced world.

The characteristics of analytical instruments produced during this period and the basic technical status of this industry at the present time are as follows:

1. The design of most products is similar to that of foreign models and some of them are the result of a combination of imitation and improvement creation; only a

very few products are of a completely new design, having no relation to foreign models.

2. In contrast to the practice of emphasizing the development of process analyzers in the previous period, much effort has been expended on the development of high-sensitivity analyzers for monitoring environmental pollution, and spectrometers for the characterization of chemical use and spectrometers for the characterization of chemical structure.

3. Some achievements have utilized various new technologies and many new types of component, e.g. some types of analytical instrument utilizing lasers have been produced and the application of research into laser remote sensing technology and tunable lasers in the field of analytical instruments has made encouraging progress. Digital display technology has been employed in many types of laboratory analytical instrumentation. The automation of analytical instruments has been improved by the application of various types of automatic control device, such as electro-magnetic valves, electronic valves, electronic timers and programmers, etc. However, no general-purpose automatic and continuous samplers have been produced. Some types of sophisticated analyzer have been equipped with dedicated mini-computers, but only a small quantity of these analyzer systems has been produced. The application of microprocessors in analytical instruments remains in the research stage. Semiconductor devices have been used extensively, and several products of all-transistorized analyzers, e.g. pH meters and infrared gas analyzers are being manufactured in batches. The appli-

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cation of integrated circuitry in analyzer products is no longer rare now-a-days.

4. Some particular components employed in analytical instrument products still cannot be manufactured in the PRC, or the specifications of those that are produced cannot meet the requirements of analytical instruments. These still have to be imported from abroad.

5. Most of the versatile laboratory analyzers produced in recent years are designed as unit blocks, part of them modular. But the assembly parts and components of similar products produced by different plants in the PRC are not unified in design and are not interchangeable.

6. With regard to reference standards for chemical components, the progress made still cannot meet the requirements for the development of analytical instruments. The demand for micro-concentration reference standards both for gases and solids is particularly urgent but, as yet, unsolved.

It can be concluded from the above-stated situation that the development of the analytical instrument industry of the PRC as a whole can hardly keep pace with developments in realizing the "four modernizations" in the PRC. The technical levels still lag far behind the advanced world levels, being equivalent approximately to the levels there in the late 60's. In future, emphasis should be laid on speeding up the application of various new technologies and new components in analytical instruments, exploring new analytical methods, strengthening scientific research and production management, and putting more effort into

achieving standardization of products, establishing reference standards and on the calibration of analytical instruments.

Papers written by the author and others /1,2/ have discussed the trend of development of analytical instrumentation in the PRC and will not be repeated in this paper.

#### CONTEMPORARY CLASSIFICATION OF ANALYTICAL INSTRUMENT PRODUCTS OF THE PRC

At present time, the concept and scope of products of analytical instruments are not unified in the world. BAII made a draft "Contemporary Classification of Analytical Instrument Products" in 1976, but it has not been effected up to now, owing to the existence of a serious divergence of opinion. Thorough discussion and reexamination of that draft is necessary before it can be put into force.

According to the definition given in the draft of the Contemporary Classification, analytical instruments are those used for analyzing Chemical components and the structures of materials. Based on the history of development and the practical status of analytical instruments in the PRC, they are classified as follows:-

- 1) electrochemical analyzers;
- 2) optical analyzers;
- 3) x-ray and  $\gamma$ -ray analyzers;
- 4) ion optical and electron optical analyzers;
- 5) thermometric analyzers;
- 6) magnetic analyzers;

- 7) chromatographs; and
- 8) miscellaneous analyzers.

Comments on this classification fall beyond the scope of this paper, but the author will adopt these criteria in this paper.

## ELECTROCHEMICAL ANALYZERS

The electrochemical analyzers produced in the PRC can be further classified as one of five groups: conductometric analyzers; potentiometric analyzers; coulometric analyzers; polarographs and automatic titrimeters.

The production of conductometric analyzers has gone on for a long period in the PRC, and basically a complete series of products with various specifications are now being produced. The main products are the DD series of process conductometric analyzers including  $\text{H}_2\text{SO}_4$ , fuming  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and microconcentrations of CO and  $\text{CO}_2$  liquid or gas analyzers and salimeters manufactured by NAIP and the Sichuang Analytical Instrument Plant (SiAIP) and DDS-11A laboratory conductometer, DDD-32B process conductometer, DDG-55 process salimeter and DDG-55A acid or base concentration meter manufactured by SSAIP.

There are several plants producing pH meters of different types designed for various applications, including laboratory, portable and process types with analog or digital display and indicating or recording meter. But these varieties are still not sufficient and the technical levels are still lower than those in some advance coun-

tries. For instance, the Model PHS-3 laboratory pH meter of SSAIP is one of the best products among its analogues in the PRC, its measurement range is pH 0-14 with a four decimal display and a precision of 0.01 pH, and the manual temperature compensation range is 0-60°C; while advanced products in the world now bear specifications as follows: measurement range, 0-14 pH, precision, 0.001 pH, manual or automatic temperature compensation with a range of 0-100°C, five decimal digital display, and can be equipped with automatic printers. In regard to the process pH meters, a typical product of the PRC is the Model PHG-21B of SSAIP, the precision of which is 0.1 pH, the stability within 24 hr is  $\pm 0.02$  pH and equipped with mechanical cleaning device for the electrodes. Not only is its performance not as good as the best products abroad, but it is also inferior in some other aspects, e.g. it does not have an ultrasonic cleaning device for the electrodes or any version of explosion-proof configurations for special applications. The varieties of electrode are much less than required, especially the lack of glass electrodes for use in uncommon ambient conditions, such as high temperature, high pressure and high viscosity samples. A series of different types of pH meter are manufactured in the PRC to meet special requirements. pH meters for use 'on board' (the instrument can stand vigorous vibration), pH meters for soil measurement, pH meters for blood samples and several types of portable pH meter for various applications are included in the list of products.

Ion-selective electrodes for measuring ions and dis-

solved gases in liquids developed rapidly in the last decade. They are characterized by high sensitivity, fast response, wide range of application, simplicity, low cost and easy operation. The number of varieties of ion-selective electrodes developed in the PRC is close to twenty, including  $K^+$ ,  $Na^+$ ,  $Ag^+$ ,  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Pb^{2+}$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $CN^-$ ,  $NO_3^-$ ,  $S^{2-}$  and  $NH_3$  electrodes [3]. However, the number of varieties now produced in batches is less than half of that. It lags behind the advanced world level in regard to both the number of varieties and their performance (e.g. selectivity and stability).

The PRC produces several types of polarograph, for example, the Model 883 pen-recording classical polarograph and Model 895 square-wave polarograph of SAIP, Model JP-1A oscillographic polarograph of Chengdu Instrument plant (CIP) and the mercury film electrode high speed polarograph of SSAIP. The performance of these instruments approaches those of advanced products in the world market. Emphasis will be placed in the future on modular design and on the improvement of flexibility and versatility. The pulse polarograph is the most sensitive of the various types and as a result of scientific research, a prototype has been worked out successfully and is expected to be put into batch production in the near future..

There are many process electrochemical analyzers, such as the Model DD-10 electric conductivity type micro  $CO$  and  $CO_2$  gas analyzer, HD-3 micro oxygen analyzer (lowest range, 0-10 ppm  $O_2$ ), DH-52 dissolved oxygen analyzer and Model JP-001 polarographic  $SO_2$  analyzer manufactured by

NAIP, and coulometric titration type micro  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_x$ ,  $\text{O}_3$  gas analyzers manufactured by BAIP, SSAIP, Wuhang Analytical Instrument Plant and Fushang Analytical Instrument Plant (FAIP). The common advantage of electrochemical gas analyzers is their high sensitivity, but the disadvantages include slow response and rather much maintenance work. A group of new sensing elements which are called the "solid state electrochemical transducers" have been developed in recent years, they retain the advantage of high sensitivity and avoid the aforesaid disadvantages /1/. Research and development in this field is progressing in the PRC. Another type of solid state electrochemical type gas sensing element - the  $\text{ZrO}_2$  solid electrolyte cell has been developed by NAIP and some research institutes. The oxygen analyzer model produced by NAIP using this sensing element is the DH-4, but the measuring range is not as wide as some other advanced products on the world market, it is not applicable for micro concentrations, and the precision is not as good as some other advanced commercial products ( $\pm 5\%$  as compared to  $\pm 1\%$ ).

Some papers have discussed the trend of development of electrochemical methods and instruments /1 - 4/, the author does not intend to repeat this here. It is expected that more achievements in research and development will be attained, and the production and application of ion-selective electrodes and solid-state electrochemical transducers will be developed with a speed higher than that for all other types of electrochemical analyzers.

## OPTICAL ANALYZERS

According to the Contemporary Classification of Analytical Instrument Products of the PRC, optical analyzers should be sub-classified into four categories, namely: dispersive light absorption, non-dispersive light absorption, light emission and miscellaneous types.

The most simple and popular spectrophotometer produced in batches since 1976 is the Model 721 spectrophotometer of the Shanghai Third Analytical Instrument Plant (STAIP) and some other plants. A prism is used as the monochromator, and the wave-length range is 360-800 nm /5/.

There are several types of UV-visible Spectrophotometers produced in the PRC. A brief description will be given of the Model 730 grating instrument of STAIP as a typical example which has been manufactured in batches since 1979. The basic specifications are as follows: range of wave-length, 200-850 nm; bandwidth, 0.2-5nm; wavelength precision,  $\pm 0.75\text{nm}$ ; linearity,  $\pm 0.75\%T$ . The characteristics of the instrument are: a special configuration of the photometer which permits a better balance of the two beams in the light path; an electric system designed to have a unique automatic zero regulating channel; multiplier high pressure negative feedback incorporated in the electric system to achieve automatic control of the whole system, only one detector for the full wavelength range, a stepping motor and a special micro harmonic gear shifter in the scan driving mechanism; a four-decimal digital display device to present the values of transmittance  $T$ , absorbance  $A$  or concentration directly, or a X-Y recorder to

plot the absorption spectrum; modular design and light structure elements are also selected in the configuration design. The technical level of this product is basically equivalent to that of advanced products in the world market in the early 70's. The Model 740 digital spectrophotometer manufactured by the same plant is an improved and simplified version of Model 730, and all the components, including gratings and photomultipliers with quartz envelopes used in this model are made in the PRC. The performance of Model 740 approaches that of Model 730, but the cost is reduced by 40%. The wavelength range of Model 710 manufactured by the SAIP and the STAIP extend from UV to near infrared, that is 190-2500nm, with a wavelength precision of 0.4nm (at 200nm) -5nm (at 700nm) and a measuring precision of transmittance of  $\pm 1\%$ . The light sources used are a hydrogen lamp and a tungsten lamp and these can be shifted automatically. A grating monochromator, photomultiplier and PbS detector are employed, and the instrument is fully transistorized.

The atomic absorption spectrophotometer is a relatively newly developed dispersive instrument, and there are several models of these instruments manufactured in the PRC now. Taking the Model WFD-Y3 of the Beijing Second Optical Instrument Plant (BSOIP) as an example, it is a single beam instrument and can be used either as an atomic absorption spectrometer or as a flame emission spectrometer. It is equipped with a logarithm converter, scale enlarger, linearization device, automatic zero setting mechanism, digital display unit and graphite furnace, and can be connected with a digital printer. Its wavelength



range is 190-900nm and the absolute sensitivity for measuring Cd with the use of a graphite furnace is  $1 \times 10^{-12}$ g. Other atomic absorption spectrophotometers made in the PRC are the Model 310 of the SAIP, Model WYZ-401 of Shenyang Analytical Instrument Plant (SuAIP) and Model YXF-1201 of BAIP.

The most interesting light source for optical analyzers is the laser, which has found wide applications in various types of optical analyzer. For instance, the use of a laser as the source gave rise to a completely novel type of Raman spectrometer /2/. Commercial laser Raman spectrometers appeared in the late 60's in the world market, and one was produced in the PRC a few years ago by BSOP /6/. The optical system of the Model WFL of BSOP is shown in Fig. 1. The light sources used include both Ar and He-Ne lasers, and the instrument is provided with liquid, solid, gas and capillary sample cells, rotating sample cell and a back-reflection device to facilitate measurement in the low wavenumber region. The wavenumber range of the spectrometer is  $2500-11800\text{cm}^{-1}$ , the precision of wavenumber indication is  $\pm 2\text{cm}^{-1}$ , and the resolution is  $1-2\text{cm}^{-1}$ .

Nondispersive infrared gas analyzers are widely used in process industries for continuous measurement of concentrations of various gases. Many products in the PRC fall into this category, such as the QGS Series of the BAIP /7/, FQ Series of FAIP /8/, HW Series of NAIP and HQG Series of SSAIP. The performance of these products is similar, the lowest measuring range is about 0-50ppm ( $\text{CO}_2$ ), the precision is usually  $\pm 2.5\%$  (high and medium

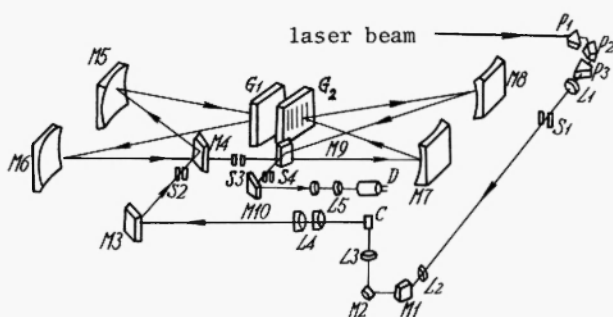


Figure 1 Schematic of Model WFL laser Raman spectrometer  
(Beijing Second Optical Instrument Plant)

D - photomultiplier; G<sub>1</sub>, G<sub>2</sub> - gratings;  
L<sub>1</sub> - L<sub>5</sub> -- Lenses; M<sub>1</sub> - M<sub>10</sub> -- mirrors;  
P<sub>1</sub> - P<sub>3</sub> -- prisms; S<sub>1</sub> - S<sub>4</sub> -- slits  
C - Sample cell

concentration) or  $\pm 5\%$  (low concentration). Some special nondispersive infrared gas analyzers for particular applications are also available in the PRC, such as the QGD Series all solid state (including light detector) infrared gas analyzer /9/ and the Model QGS-06 all solid state gas analyzer, for measuring CO<sub>2</sub> in expiration, manufactured by BAIP, Model SH-W of FAIP /10/ and Model QGD-07 of BAIP /11/ portable infrared gas analyzers for agricultural applications, and infrared gas analyzers equipped as a part of the Model KH-01 automatic infrared controller of the BAIP for automatic control of carbon permeation treatment /12/. Although several versions, specifications and models of infrared gas analyzer are being produced in the PRC, the sensitivity, precision and stability of the

instruments are usually not equal to the best products abroad. Efforts are being made in the PRC to improve this situation.

A typical emission spectrometer is the Model WLP-8 direct reading spectrometer manufactured by the SuAIP and Shanghai Optical Instrument Plant since 1976. Its wavelength range is 220-410nm with 12 channels, three of which are for internal calibration, the maximum number of elements that can be measured simultaneously is 11.

Temperature compensation is incorporated in the instrument, so that it operates normally without the need of a thermostat if the variation of ambient temperature does not exceed  $\pm 3^{\circ}\text{C}$ . The analysis time required for an individual sample is about 2-3 minutes, and the repeatability is within  $\pm 0.5\%$ . The grating used is 40x60mm in size with 1200 lines per millimeter. The instrument can be operated continuously for 8 hour shifts.

Fruitful results have been achieved in research and development of a correlation spectrometer and remote sensing techniques by the use of laser (or LIDAR). It is reasonable to predict that these technologies will result in the production of commercial instruments in the PRC in the near future.

The tendency to use tunable lasers and microcomputers are no doubt two of the most important trends in the future development of optical analyzers /1,2/.

## MASS SPECTROMETERS

The main applications of mass spectrometers include qualitative and quantitative chemical analyses of solids, liquids and gases, isotope-ratio analysis, structural analysis and leak detection for vacuum systems. The modes of analyses include bulk analysis, surface microanalysis and surface scanning analysis, depth microanalysis and depth scanning analysis, etc. They are becoming more and more important analytical tools since they are characterized by high sensitivity, high accuracy and wide range of application. The combinations of m.s. with chromatographs is one of the most effective analytical tools ever known.

During the late 50's and early 60's the Atomic Energy Institute and the Geology Institute of the Academy of Sciences of China (ASC) and the Beijing Geology College did some research work separately on developing a Nier type m.s. /13/. The development of Model ZhT - 1305 m.s. for analyzing isotope ratios was carried out by the BAIP and Beijing Scientific Instrument Plant (BSIP) of ASC from 1960 to 1962 /14/. It was modelled on a Russian instrument, Model MM - 1305, and played an important role in isotope-ratio analysis at that time. Model ZhH - 1301 m.s. for the chemical analysis of gases was produced in 1965 by the BAIP /13/. The same plant was successful in developing a prototype quadrupole mass filter Model ZhL - 01 in the same year (its improved version Model ZhL - 02 was produced in 1966), thus China became the third earliest country which manufactures this type of instrument /14/. A prototype spark source double-focusing

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m.s. was developed by the BSIP in 1966. Another prototype of spark source double-focusing m.s., Model ZhP-G-A, was developed by the BSIP and Shanghai Electron Optics Institute. An improved version Model ZhP-G-A1 was manufactured by the Xinyue Instrument Plant (XIP) in Shanghai, and another improved version, Model ZhP-2, was manufactured by BSIP.

Model ZhT - 02 m.s. for isotope-ratio analysis produced by BAIP in 1976 is an improved version of ZhT-1301. The performance of the former is significantly better than the latter. For instance, the mass range is expanded from 1-400 to 1-1000 atomic mass unit, the resolution is improved from 300 to 370, and the sensitivity is raised from  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  A/torr. To satisfy the demand for the analysis of stable gas isotope-ratios, Model ZhT-03 m.s. was developed by the BAIP in 1978 /15/. It was suitable for precise measurement of the abundance ratio of isotopes  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{18}\text{O}/^{16}\text{O}$  and  $^{34}\text{S}/^{32}\text{S}$ ; the precision of measurement is 0.02% and the sensitivity is  $1 \times 10^{-3}$  A/torr for nitrogen.

In the area of residual gas analysis, the Model ZP-4001 quadrupole partial pressure meter was developed by BAIP in 1976. The minimum detectable partial pressure was an order of magnitude lower than its predecessors, Model ZhL-01 and Model ZhL-02.

The production and application of g.c./m.s. has been accelerated since the first commercial instrument was put on the market by LKB Ltd., of Sweden in 1965, and the technique is now becoming a sophisticated routine one for

laboratory use. Being influenced by the political upheaval since 1966, the first g.c./m.x. Model ZhD-01S of PRC was not developed until 1976 by BAIP /16, 17/. The prototype of Model SZJ-1 g.c./m.s./ was developed by the BSIP, Dalian Chemical Physics Institute (DCPI) and the Shenyang Automation Institute in 1977 /18/. Both mass spectrometers are 60° sector magnetic type instruments, and the g.c./m.s. interfaces of both are two-stage jets made of stainless steel. The function of the computer data processing system of Model SZJ-1 include reference sample (PEK) intake for mass scaling, calculation of the mass number (within the mass range of 10-500 a.m.u.) of the peaks by using the mass scale, background deduction, normalization, storing of multi-scanning mass spectra, printing of the mass number-relative peak strength relation, bar graph of mass spectra and the values of the eight largest peaks.

The surface and depth analysis of materials is becoming more important in the field of physics, metallurgy, biology, medical sciences, quality control of various kinds of materials etc., and thus surface and depth microanalyses have emerged as an important branch of instrumental analysis. Microanalyzers based on m.s. are amongst the most important surface and depth microanalyzers. Model ZLF-300 developed by XIP in 1976 is an ion mass analyzer of the direct imaging type /13/. The Model LT-1 scanning ion probe mass microanalyzer /13/ first produced by the BSIP in 1978 is applicable to thin film surface analysis, depth analysis and isotope-ratio analysis; the

diameter of the area to be analyzed is adjustable continuously from 2 to 200 nm.

In addition, several types of mass spectrometric leak detector are manufactured in the PRC, such as the Model ZhS-21 produced by CIP since 1969.

A prototype process m.s. was developed and applied to an oxygen top-blown converter in the late 60's. Ions of different mass-to-charge ratio are separated by a  $180^\circ$  homogeneous magnetic field mass analyzer, and up to four of them are collected simultaneously by four collectors (Faraday cups).

Table 1 summarises and lists the applications, names of manufacturers, the years of prototypes developed and some main technical specifications of the m.s. products of the PRC. The reference numbers are listed for those who would be interested to obtain further information.

#### CHROMATOGRAPHS

There are several factories manufacturing different types of chromatograph in the PRC, including BAIP, SAIP, SiAIP, NAIP, Lunan Chemical Instrument Plant (LCIP, formerly Tengxian Second Radio Factory), Beihai Instrument Plant (BIP), Dalian Second Instrument Plant (DSIP) and Waihai Balance Instrumentation Plant. The earliest commercial GC products were manufactured by BAIP in 1963. The number of GC instruments produced in the PRC was estimated about 15,000 till 1979, over half of which were produced by the BAIP.

TABLE 1 -- M.S. PRODUCTS OF PRC

Name of Product	Model	Applications	Manufacturer	Year of prototype developed	Main Technical Specifications			Reference No. and Remarks
					Mass Range (a.m.u.)	Resolution (10% valley)	sensitivity precision	
m.s. for isotope-ratio analysis	ZhT-1301	isotope-ratio analysis of solids and gases	BAIP	1962	1-400	300	$1 \times 10^{-5}$ A/torr Single beam: $\pm 1.0\%$ Double beam: $\pm 0.2\%$	14; production ceased
	ditto	ditto	BAIP	1976	1-1000	350	$1 \times 10^{-4}$ A/torr Single beam: $\pm 0.5\%$ Double beam: $\pm 0.05\%$	
m.s. for stable isotope-ratio analysis	ZhT-03	analysis of stable gas- eous isotope-ratios	BAIP	1979	26-100	70	$1 \times 10^{-3}$ A/torr 0.02%	15
m.s. for chemical analysis	ZhT-1301	analyses of gases and isotope-ratios	BAIP	1965	1-80	80	relative sensitivity: $2 \times 10^{-4}$	13; production ceased
quadrupole mass filter	ZhT-01	residual gas analysis	BAIP	1965	2-100	100	min. detectable partial pressure: $2 \times 10^{-10}$ torr	



TABLE I (cont)

Name of Product	Model	Applications	Manufacturer	prototype developed	Main Technical Specifications			Reference No. and Remarks
					Mass Range (a.m.u.)	Resolution (10% valley)	sensitivity	
ditto	ZHL-02	ditto	BAIP	1966	2-100	200 (50% valley)	min. detectable partial pressure: $1 \times 10^{-10}$ torr	14
ditto	ZP-4001	ditto	BAIP	1976	1-150 10-400	250 300	min. detectable partial pressure: $5 \times 10^{-12}$ torr	$\pm 2\%$
direct-imaging type ion mass analyzer	ZLF-500	surface & depth elemental microanalyses	XIP	1976	1-300	1000	$10^{-6} - 10^{-9}$	13, 14; X, Y resolution: 1-2 nm; space resolution: 5-10 nm
ion probe LT-mass spectrometric micro-analyzer	LT-1	ditto	BSIP	1978	1-300	>1000	$2 \times 10^{-8}$ (8 in Si)	18; space resolution <2 nm; diameter of primary beam <2 nm.
space scanning double-focusing m.s.	ZHP-2	analysis of trace amount of impurities in solids	BSIP	1970	1-240	>2000	$10^{-8} - 10^{-9}$	13

TABLE 1 (cont)

Name of Product	Model	Applications	Manufacturer	prototype developed	Main Technical Specifications				Reference No. and Remarks
					Mass Range (a.m.u.)	Resolution (10% valley)	sensitivity	precision	
ditto	ZhG-6-Al	ditto	XIP	1970	1-1000	2000	$10^{-8}-10^{-9}$		13
g.c./m.s.	ZhO-01S	analysis of organic compounds & structural analysis	BAIP	1976	1-2000	5000	$1 \times 10^{-10}$ g/s (methyl stearate)	stability of total ion current: $>5\%$ (in 10 min.)	16,17
g.c./m.s./Comp.	SZJ-1	ditto	BSIP	1977	10-2000	800	$10^{-7}$ g	precision of mass scaling: $\pm 0.4$ a.m.u.	18
process (mag-netic type)	proto-type	simultaneous analysis of up to 4 components in exhaust gas of oxygen top-blown converter	BAIP	1969	12-44	50	$10^{-5}$ A/torr (Ar)	1.5%	14

A common characteristic of the most sophisticated products, such as SP-2308 of BAIP, Model 103 of SAIP, Model SP-501 of LCIP and SP-08 of DSIP is their ability to provide several types of sampler, column and detector, and a series of support accessories for better performance and versatility. For instance, Model 103 is characterized by a dual-flow system with a multi-stage oven temperature program control, offering a choice between packed column and capillary column and between five different types of detector, i.e. TCD, FID, ECD, FPD and TSD, and also offering a lot of support accessories including high-frequency pyrolyzer and small-scale preparative accessories. Model SP-2308 is characterized by a dual-column system with a choice of four types of detector including TCD, FID, ECD and FPD, multi-stage oven temperature program control, an all-glass chromatographic system, which greatly minimised contamination during the course of microanalysis, and the integration of vaporizer, column and detector to constitute a whole system known as an "analytical block" to reduce the dead volume to a minimum so as to lower the "off-column effect" which would affect the column efficiency greatly.

All commercial gas chromatographs in the PRC are provided with one or two sets of TCD and/or FID. The sensitivity of TCD is around 2000 mV·ml/mg or less (benzene with H<sub>2</sub> as carrier gas), and the detectability of FID is generally equal to or better than 10<sup>-11</sup>g/s (benzene).

New achievements in developing novel gas chromatographic detectors have been characteristic of chromatogra-

phic technology in the PRC. ECD is extremely sensitive to halides and is very useful for detecting residual pesticides and some kinds of drugs and drug metabolites. In the past, deuterium was used as the radioactive source of ECD, hence the detector was non-applicable to the analysis of sample components with b.p. higher than 200°C. The new ECD incorporated in Model SP-2308 utilizes a  $^{63}\text{Ni}$  source, the operating temperature of which can be as high as 350°C. As shown in Fig. 2, it is a coaxial single electrode cylinder type with its radioactive source connected to earth.

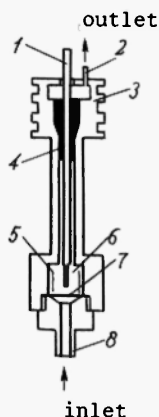


Figure 2 Schematic of  $^{63}\text{Ni}$  ECD (Beijing Analytical Instrument Plant)

- 1 - collector; 2 - vent; 3 - radiator;
- 4 - PTFE insulator; 5 -  $^{63}\text{Ni}$  source;
- 6 - ionization chamber, 0.8 ml in volume;
- 7 - stainless steel gauze;
- 8 - base, earthed.

The detector is powered by a pulsed voltage source with the amplitude and duration of the pulse fixed and the period of pulse adjustable, thus the signal-to-noise ratio and linearity of the detector is improved, and is adaptable to wide range of samples. The linear range and detectability are respectively  $10^3$  and  $5 \times 10^{-13} \text{g}$  for lindane. With the application of the constant-current pulse-modulated operation mode, even higher sensitivity and better linearity can be obtained. When the capture effect is caused by the sample, the pulse frequency is changed automatically to maintain the detector current constant, and the value of the frequency change will be a measure of the concentration of the component to be analyzed. This technique has been adopted by several research institutes such as the Shanghai Insects Institute, and is expected to be applied to commercial products in the near future.

The FPD is widely accepted in residual pesticide analysis for its selective response to compounds containing sulphur and phosphorus. The performance of the FPD of Model 103 or Model SP-2308 (Fig. 3) approaches that of the best products in the world, e.g. the detectabilities for S and P are  $10^{-10} \text{g/s}$  and  $10^{-12} \text{g/s}$  respectively, and the sample quantity permitted may be up to  $40 \mu\text{l}$ . a novel type of dual-flame FPD was developed by the Shantong Institute of Chemistry and manufactured by the LCIP. The operation of a dual-flame eliminates the interference of hydrocarbons or other solvents and improves selectivity and response to sulphur-containing compounds. Its principle of operation is that the sulphur- and phosphorus-containing

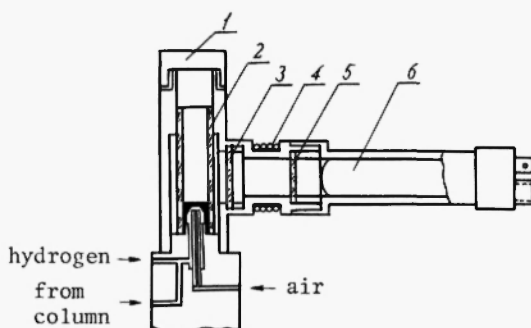


Figure 3 Schematic of FPD (Beijing Analytical Instrument Plant)

- 1 - venting hood;    2 - flame chamber;
- 3 - quartz window;   4 - cooling water coil;
- 5 - filter;            6 - photomultiplier

components are burned in the oxygen-rich flame of the lower jet together with the solvent components, and the products of combustion of the S- and P-containing components are then reduced to  $S_2$  and  $HPO$  respectively in the hydrogen-rich flame of the upper jet with the emission of characteristic radiations peaking at 394 and 526 nm respectively.

The thermionic specific detector (TSD) is specific to N- and P- containing components, and is, therefore, known as the nitrogen-phosphorus detector (NPD). It is a valuable detector. The detectability of the TSD of Model 103 manufactured by the SAIP is  $8 \times 10^{-11} \text{ g/s}$  (trimethyl phosphate). However, the comparatively short life of TSD presents an obstacle to its further application. DCPI has partly solved this problem recently. The TSD developed

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by DCPI is incorporated with a special rubidium bead which lasts longer than the previous designs in the PRC.

High pressure liquid chromatographs have been produced in the PRC since 1975 and approximately 500 sets had been manufactured up to 1979. Table 2 gives a brief description of the models produced. It can be seen from Table 2 that the performance of the HPLC products of the PRC are not ideal from the following points of view: the number of types of detector is quite limited, especially lack of a variable-wavelength UV detector and fluorescence detector, the elution modes are only limited to isocratic and linear gradient programming, the pumping system is not stable enough and the operating pressure is limited to lower than  $150 \text{ Kg/cm}^2$ , no sophisticated data system is available and the operation is not so easy and reliable, especially as compared with the microcomputer-based HPLC products manufactured abroad.

Efforts have been made to improve the performance of the individual components of HPLC, including column, detector pumping system, data system, etc., and fruitful results have been obtained. As an example, it is worthwhile to note that a high-efficiency microparticle column has been developed by DCPI and the Shanghai Reagent Institute. The particle size is 5-10 nm and the efficiency can be as good as  $4 \times 10^4 - 8 \times 10^4$  theoretical plates/meter.

#### OTHER CATEGORIES OF ANALYZERS

It is impossible to describe all the categories of analytical instruments of the PRC in detail in this paper.

TABLE 2 - LC PRODUCTS OF PRC

Type	Model	Manu- facturer	Year of Prototype Developed	D e t e c t o r s			P I	P r e p a r a t i o n		Reference: No. and Remarks
				UV noise (abs.unit)	RI drift (RI units per hour)	IC detectability(g/s)		Operating pressure (kg/cm <sup>2</sup> )	Elution Mode	
HPLC	SY-01	BAIP	1975	$\pm 2 \times 10^{-4}$	-	-	-	pneu- matic	isocratic	15; RI & DC detec- tors avail- able since 1979
HPLC	SY-01A	BAIP	1979	$\pm 2 \times 10^{-4}$	$10^{-6}$	$6 \times 10^{-5}$ (nitrobenzene in n-heptane)	-	pneu- matic	isocratic & linear gradient program- ming	15; eluate collector accessory available
HPLC	150	SAIP	1976	$\pm 2 \times 10^{-4}$	$10^{-6}$	-	$2.1 \times 10^{-8}$ (squalene) mat:	pneu- matic	isocratic 20	
HPLC	SY-201	SAIP	1979	$\pm 2 \times 10^{-4}$	$1.6 \times 10^{-5}$	-	-	pneu- matic	isocratic & linear gradient program- ming	
HPLC	CX-801	NAIP	1979	$\pm 2 \times 10^{-4}$	-	-	-	dual-ram recipro- cal	isocratic 15	
gel per- meation chroma- tograph	SH-01A	BIP	1977	-	$2 \times 10^{-6}$	-	-	dual-ram 0-20 recipro- cal	isocratic	



Instead, the author intends to run-through all the other categories of analytical instruments not mentioned above.

According to the Contemporary Classification of Analytical Instruments of the PRC, four types of analyzer fall into the category of magnetic analyzers, i.e. thermo-magnetic, magneto-dynamic, nuclear magnetic resonance and electron paramagnetic resonance types. A series of magnetic oxygen analyzers of various specifications were produced in the PRC, such as CD series and QZS Series thermo-magnetic oxygen analyzers manufactured by NAIP and BAIP respectively and CJ Series magneto-dynamic oxygen analyzers manufactured by SiAIP. The only PRC-made n.m.r. available on the market is the Model BH-2 60 MHz high resolution n.m.r. of BAIP since 1977/21/, which is an improved version of Model BH-1 developed in 1974 /22/. Model BH-2 can be used to detect  $^1\text{H}$  and  $^{13}\text{F}$  nuclei, its resolution is better than 0.6 Hz, and its sensitivity is higher than 30:1 (1% solution of ethyl benzene in  $\text{CCl}_4$ ). No e.p.r. product is available from the PRC yet.

Thermometric analyzers can be further divided into three groups: thermo-conductivity, thermo-chemical and differential thermometric types. There are many available on the market in each group, especially since the production of the former two has been undertaken for about 20 years, and the processing technology of these instruments is relatively mature. There are several series of these analyzers in production, such as the thermo-conductivity gas analyzers (RD Series) of NAIP and SiAIP /23/, the QRD Series of BAIP and the thermo-chemical gas analyzers (RH Series) of NAIP and SiAIP /24/. There are also

several differential thermometric instruments on the market, including the differential thermal analyzers of the Beijing Optical Instrument Plant and the vacuum differential thermal analyzers of the Dandong Precise Instrument Plant.

Several different types of x-ray analyzer have been produced in the PRC, such as the Model XYS-1 x-ray diffractometer of SSAIP /25/, the Model G1-1 x-ray fluorescence spectrometer, Model 2 x-ray diffractometer, Model JF-1 x-ray crystal analyzer and four-channel x-ray fluorescence spectrometer for slurry process analysis (prototype) of the Dandong Instrument Plant, and the Model DXY-3 multi-channel x-ray spectrometer of XIP. The performance of some of these approaches that of the best products in the world. Taking Model DXY as an example, the range of elements detectable is  $^{11}\text{Na}$  -  $^{92}\text{U}$ , the current and voltage stability is 0.03%, and the high-voltage stability of the detector is 0.02%. There are four interchangeable analyzer crystals and seven channels (two of which are scanning channels). By choosing appropriate optional accessories, it can be used as a diffractometer. A dedicated minicomputer is used for data processing. In general, this is one of the best x-ray analyzers manufactured in the PRC. Unfortunately, some necessary components including some kinds of organic crystals with large lattice spacing, solid-state detectors and high-power rotating-target x-ray tubes can not yet be produced in the PRC, and this seriously hinders the further development of x-ray analyzers.

Many analyzer products which cannot be classified in

any of the preceding classes fall into the category of "miscellaneous analyzers". This consists of a wide range of different groups of analyzers. Each group of analyzers may work on the same principle or for similar applications. In the group of gas-in-metal (or alloy) analyzers, there are at least three models of oxygen-in-metal analyzer in the PRC, viz., Model GXH-902 of BAIP, Model GHM-201 of FAIP /26/ and Model SQM-1 of the Dalian Second Electronic Instrument Plant /27/. Hygrometers represent a group of analyzers devoted to the analysis of humidity. Many types of process hygrometer are produced in the PRC, such as coulometric hygrometers manufactured by BAIP and CIP, dry-and-wet-bulb type hygrometers manufactured by BAIP and the lithium chloride type dew point controller manufactured by CIP /28/. Some analyzers specially designed for medical use may fall into the category of miscellaneous analyzers, such as multi-channel blood analyzers and expiration gas analyzers manufactured by BAIP and NAIP. The Model PC-01 dust-in-air meter manufactured by BAIP is the only product in the group of piezoelectric crystal type analyzers to date; the operation principle of this group of analyzers is unique and different from any other analyzers or other groups in the same category. The dust in the air sample is collected on an A/T cut quartz crystal, and the deviation of the natural frequency of oscillation gives a measure of the mass of the dust deposited.

## ANALYZERS FOR POLLUTION MONITORING

Before concluding this paper, it is worthwhile to give a general picture of the analyzer products of the PRC for pollution monitoring, which developed rapidly in the last decade. These analyzers are not covered in a single category or group in the Contemporary Classification of Analytical Instruments, but spread over various categories according to their own working principles.

The DK Series of coulometric analyzers of the BAIP operate on the principle of dynamic coulometric titration. Taking Model DK-6301 /30/ as an example, its cell consists of three electrodes: a platinum wire anode, a platinum wire cathode and an active carbon reference electrode and contains a 0.3M alkaline solution of KI. The current that flows through the reference electrode is a measure of the  $\text{SO}_2$  concentration of the air sample. The instrument is very sensitive; a 1mA reference electrode current is equivalent to  $0.08 \text{ mg SO}_2/\text{M}^3$  and the minimum detectable concentration is  $0.025 \text{ mg}/\text{M}^3$ . Model DK-9001 /31/ and Model DK-5201 /32/ manufactured by the same plant are used to detect  $\text{NO}_x$  and  $\text{O}_3$  and total oxidants respectively.

The disadvantage of the coulometric analyzer is its relatively slow response and requirement for maintenance. Therefore, it is gradually giving way to other analyzers based on other physical principles, such as the chemiluminescent  $\text{NO}_x$  analyzer Model HGS-802 of the SSAIP /33/ developed in 1978 and the chemiluminescent  $\text{O}_3$  analyzer

Model GSH-201 and the chemiluminescent  $\text{NO}_x$  analyzer Model GSH-202 of BAIP developed in 1979. The minimum detectable concentration is  $0.005 \text{ mg O}_3/\text{m}^3$  for Model GSH-201 and  $0.02 \text{ mg NO}_x/\text{m}^3$  for Model GSH-202.

On the basis of the production of a whole range of air pollution monitoring analyzers, a prototype of an air pollution monitoring van was developed in 1978 by BAIP with the assistance of a number of institutes, colleges and plants /34/. The analytical instruments with which it is equipped include the Model DK-6301  $\text{SO}_2$  analyzer, the DK-9001  $\text{NO}_x$  analyzer, Model DK-5201  $\text{O}_3$  and total oxidant analyzer, Model PC-01 dust-in-air meter and Model ST-01 g.c. for analyzing  $\text{CO}$ ,  $\text{HC}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ . A data processing system, Model F2002, is also included.

With regard to the monitoring of water pollution, SSAIP has developed a series of analyzer systems - the Model SJG-702 water quality monitor /35/. The parameters monitored include pH, dissolved oxygen, electric conductivity, oxidation-reduction potential and temperature. The dissolved oxygen meter used is a polarographic type analyzer with a gold cathode and an  $\text{Ag-AgCl}$  electrode as its anode. A polyethylene membrane (20 nm thick) is used to separate the  $\text{KCl}$  electrolyte from the water sample. Dissolved oxygen in the water sample diffuses through the membrane and is reduced at the cathode, and this causes a diffusion current to flow between the electrodes, which can be taken as a measure of the dissolved oxygen concentration of the water sample. The range of measurement is 0-20 ppm, and the precision is  $\pm 1 \text{ ppm}$ .

List of Abbreviations of Manufacturers and Research  
Institutes which appear more than once in this paper

ASC	Academy of Sciences of China
BAIL	Beijing Analytical Instrument Institute
BAIP	Beijing Analytical Instrument Plant
BIP	Beihai Instrument Plant
BSIP	Beijing Scientific Instrument Plant
BSOIP	Beijing Second Optical Instrument Plant
CIP	Chengdu Instrument Plant
DCPI	Dalian Chemical Physics Institute
DSIP	Dalian Second Instrument Plant
FAIP	Fushan Analytical Instrument Plant
LCIP	Lunan Chemical Instrument Plant (formerly Tengxian Second Radio Factory)
NAIP	Nanjing Analytical Instrument Plant
SAIP	Shanghai Analytical Instrument Plant
SSAIP	Shanghai Second Analytical Instrument Plant
STAIP	Shanghai Third Analytical Instrument Plant
ShAIP	Shenyang Analytical Instrument Plant
SiAIP	Sichuan Analytical Instrument Plant
XIP	Xinyue Instrument Plant

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