A MINIATURE MASS SPECTROMETER FOR HYDRAZINE DETECTION

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ABSTRACT

A Miniature Mass Spectrometer (MMS) with a focal plane (Mattauch-Herzog) geometry has been developed at the Jet Propulsion Laboratory (JPL). The MMS has the potential to meet the NASA requirements of 10 parts per billion (ppb) sensitivity for Hydrazine detection, as well as the requirements for instant response, portability, and low maintenance. As a focal plane mass spectrometer, it can be used as a universal hazardous gas detector.

The unit has demonstrated a sensitivity of 400 ppb with benzene. The objective of the current work is to increase the sensitivity to 10 ppb of Hydrazine in air. The sensitivity has been increased with a new ionizer which increased the total ion density by a factor of 10. A high voltage power supply has been built to further increase the sensitivity by increasing the voltage from 600 volt to 1450 volt. Testing of the new power supply is currently underway.

Kennedy Space Center has a Standard Gas Generator with the unique capability of generating a calibrated stream of 10 ppb of Hydrazine in air. After the JPL tests are completed, the MMS will be tested in the KSC facility.

I INTRODUCTION

Hydrazine and related compounds are used in NASA/AF space programs and in F-16 aircraft. The fueling of spacecraft, the Space Shuttle, and rockets with Hydrazine type fuels is a very hazardous operation and lightweight portable Hydrazine detectors are needed to monitor the work environment. The exposure limits are now 10 ppb (8-hour Time Weighted Average) for Hydrazine, Mono Methyl Hydrazine and Unsymmetrical Di Methyl Hydrazine.

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JPL published a report (Ref. 1, 2) with the results of a survey to find a sensor that could measure hydrazine compounds down to 10 parts per billion with instant response in a working environment atmosphere. The report identified a tunable laser diode IR system (Ref. 2) as a potential sensor that can meet most of the requirements for an instrument. Experiments carried out on a space flight prototype at JPL showed a suitable wavelength and a satisfactory sensitivity. However, the instrument would be rather heavy, 20 lbs, and the cost would be high.

Another sensor that was identified as having the potential of meeting the requirements, including the weight and cost criteria, is the electronic nose concept. However, the sensor has potential response and saturation problems. Work is underway at KSC to test this concept further.

A new leading candidate for a 10 ppb portable Hydrazine detector has now been identified in the area of Miniature Focal Plane Mass Spectrometry. A mass spectrometer is a useful general instrument that can measure almost any volatile compound, including other fuels, as well as oxidizers. A portable miniature mass spectrometer can be used as a universal hazardous gas detector. The FBI has shown an interest in such a portable high sensitivity hazardous gas detector.

An instrument is under development at JPL to measure the contaminants in the air of the space station. In this task the focal plane mass spectrometer has been improved in sensitivity by the use of a new ion detector array. The size has been reduced by an order of magnitude by using a new material for the permanent magnet. The result is a laboratory unit that measures 6 inches in length. This new instrument (Figure 1) currently exists as a "table top" device, mounted inside a vacuum bell jar (Figure 2).

This development has the potential to meet the NASA critical criterion of 10 ppb sensitivity of Hydrazine, portability, immediate response, acceptable cost, and low maintenance. The demonstration of this technology to measure 10 ppb of Hydrazine in air is the main thrust of the Hydrazine Detection task in FY 2003. Assuming success, a prototype instrument can be built in FY 2004 by an outside instrument manufacturer. Two companies have already expressed interest in this new technology. One company has been licensed by Caltech to develop the new technology for commercial applications.

It is very difficult to build a reliable source of sample air containing 10 ppb of Hydrazine. Such a sample source is needed to check out new Hydrazine detectors. KSC has successfully developed and tested such a unit as part of their Hydrazine detection work. The JPL Miniature Mass Spectrometer will be tested at KSC using the KSC Test Gas Generator. Agreement has been reached with KSC to carry out such tests at KSC as part of their work on Hydrazine Detectors at NASA.

To meet the need for space qualified parts in using the Miniature Mass Spectrometer in the Space Station or the Space Shuttle, work is planned at JSC to carry out analysis and tests for space qualification of the instrument.

The task of developing the Miniature Mass Spectrometer is thus a cooperative effort between JPL, KSC and JSC. A Memorandum of Understanding has been developed that summarizes the task elements and it was reviewed by NASA Code QS and signed by the parties in 2001.

II TECHNICAL METHODOLOGY/APPROACH

A Miniaturized Mass Spectrometer (MSS) with an array detector for measurement of ion intensities has been developed at the Jet Propulsion Laboratory. The spectrometer has a focal plane geometry, and can measure the intensities of different masses simultaneously. The array detector has a resolution of 25 micrometers and is based on the ion-electron-photon process.

The instrument was designed for use in the Space Station to measure low concentrations of chemicals that build up in the air. A sensor with high sensitivity, specificity, fast response time, and applicability to a wide range of contaminants is needed to monitor the air quality of the habitat. A miniature Gas Chromatograph (GC) was incorporated in this instrument to separate the various contaminants before entry into the mass spectrometer.

This instrument can be easily adapted for measuring Hydrazine in air at the 10 ppb level. In the case of Hydrazine detection the GC section would provide extra residence time in the GC column where absorption and decomposition of the Hydrazine will take place. Hydrazine is very prone to rapid decomposition in air and it was decided to eliminate the GC section. The sampled air can be admitted directly into the vacuum environment of the ionizer of the Mass Spectrometer for instant response and minimal decomposition and absorption of the hydrazine. A new high sensitivity ionizer has been procured for the MMS as the current one is not designed for high sensitivity.

The following description of the various new components in the MMS will outline how the performance and the low mass were obtained.

The analyzers are, in general, of two kinds: scanning and non-scanning. The focal plane mass spectrometer is essentially a non-scanning type and it measures the intensities of all masses simultaneously. The sensitivity of a non-scanning MS is inherently greater than that of a scanning type (e.g. a quadrupole MS) because the latter measures the signal at a given mass peak only for a short dwell time. In contrast, a non-scanning MS measures all mass intensities during the entire time of signal generation from the analyte. This type of measurement is equivalent to single ion monitoring at all masses simultaneously.

In a scanning mass analyzer (e.g. a quadrupole mass spectrometer) the ions of one mass are separated for their measurement while the signal ions of all other masses are discarded. The measurements of different mass ions are done successively in time. This mode of signal measurement thus makes use of a small portion of the total signal. This type of mass analyzer, therefore, has a very low duty cycle. In the non-scanning type of mass analyzer, the ions of different masses are spatially separated and their intensities are measured simultaneously by an array of detectors. This type of mass analyzer provides a duty cycle of 100 %. A non-scanning mass spectrometer possesses higher sensitivity as compared to the above-mentioned scanning type of mass spectrometers. Simultaneous measurement of all masses is equivalent to taking a photograph of the mass spectrum. This feature enables the measurement of the mass spectrum of fugitive samples that may not last long enough in the ion source for the measurement of the complete mass spectrum with a scanning type of mass spectrometer. The 100 % duty cycle obtained by simultaneous measurement of all masses makes a non-scanning mass spectrometer uniquely suited for measurements requiring high sensitivity.

In the past, the lack of a detector with high gain (such as an electron multiplier), and the lack of spatial resolution for a non-scanning MS have restricted its application for measurements that required high sensitivity. A photographic plate was used for the ion detection. Also, the large weight of the magnetic sector of a mass spectograph has made it impractical for field use.

In the JPL Miniature Mass Spectrometer (Figure 1) the magnetic sector is made of the new Nd-B-Fe alloy (energy product of 45-50 MGOe) instead of the previously used material Alnico V (energy product of 5-7 MGOe). This resulted in a reduction of the mass of the magnet by an order of magnitude. The yoke was fabricated from a high saturation flux (2.2 kG, Hiperco-50A V-Ni-Fe alloy) to minimize its mass.

The electrostatic sector is fabricated from a single piece of ceramic (MACOR). The design eliminates the problems associated with the alignment of the electric sector rails, and facilitates the alignment of the electrostatic sector with the magnetic sector.

A new ion detector (Figure 3) was developed for the simultaneous measurement of the intensities of different mass ions. The array detector is based on the conversion of ions into electrons into photons sequence and their final measurement by a photon array detector. The linear array detector, called an electro-optical ion detector (EOID), comprises a micro channel plate (MCP), a phosphor coated fiber optic window, and a photodiode array.

The MCP is located a distance of 25-100 micrometers from the phosphor plate. The close proximity of operation is made possible by using a low energy excitation of phosphor. For this purpose, a phosphor like ZnO: Zn is used. Such a phosphor provides two main advantages: phosphorescence can be efficiently excited at lower electron energies (50-500 eV), and the inherent excess O-vacancies make this phosphor conductive. Therefore, no conductive layer of aluminum is used like in older JPL designs. The phosphor plate was coated with a layer of Indium Tin Oxide (ITO). The ITO layer is

optically transparent, and electronically conductive. It provides a conductive path for the electrons, and allows the transmission of the phosphorescence signal.

All the components of the Miniature Mass Spectrometer (ion source, electrostatic sector, magnetic sector and the detector) are mounted on a single base plate (see Figure 1), thus making it rugged and simple to align. Overall, the result is a compact design. It is estimated that the MMS will possess a total mass of 700-800 g after interfacing it with miniaturized electronics and an ion vacuum pump. A vacuum tight enclosure and a power supply with a battery for a load of 2-4 watts are to be added to this, resulting in a total estimated mass of say 1500-2000 g (3-4 pounds).

IV OVERALL TASK PLAN

This year's task is to improve the sensitivity of the existing tabletop instrument and to measure its performance at JPL and KSC. The next year' s work should result in a prototype of the new MMS instrument built by a commercial contractor. The prototype will be tested extensively at KSC in the third year. This prototype can then be the basis for space qualification work and for commercial production of the instrument.

V RECENT WORK

New Ionizer

A new ionizer was procured to improve the sensitivity of the instrument. The sensitivity of the MMS has been measured before by direct introduction of benzene vapor into the MMS. The sensitivity with benzene was 400 ppb with a signal to noise ratio of 2.
The new ion source was designed to have high efficiency of ionization and ion collection. With the new ionizer the ion intensity as measured with a Faraday Cup was 6 microamp / torr, a factor of 30 higher than with the older ion source. Another measurement was made with the Faraday cup along the flight path just before the magnetic sector. This measurement showed a gain of a factor of 10. The next measurement is to measure the signal with the array detector.

Higher Voltage Power Supply

Another way of increasing the sensitivity is to increase the number of ions that are generated in the ionizer. This will result in a stronger signal and increased sensitivity. An increase in the number of ions can be accomplished by increasing the voltage. A new power supply was designed to increase the voltage from 600 volt to 1450 volt. The expected range of operating voltages will be 1100 to 1200 volt.

The power supply was also designed for increased stability and flexibility, with 15 independently controlled voltages and individual noise filters. The 15 voltages can be independently changed to arrive at an optimum performance for the overall instrument.

The voltages can be changed with individual potentiometers on the front plate of the power supply and the voltages can be measured and monitored by means of individual test points on the front plate.

Another feature is a filament current limit to prevent filament burn-out such as has happened on a sudden increase in pressure in the unit. There are 2 filaments available in the ionizer in case that one does not work after a mishap.

The new power supply has been completed and is currently being checked out. Figure 4 shows a.photograph of the power supply with the individual potentiometers and the individual test points for the 15 voltages.

VI FUTURE WORK

After checking out the operation of the power supply with the MMS, an optimization procedure will take place to find the optimum voltages to obtain the highest sensitivity. The initial work will be done with residual gas (air), followed by measurements on benzene , ammonia and hydrazine.

Once a satisfactory sensitivity has been obtained, the instrument (and the bell jar) will be packaged and shipped to KSC for further testing with the Standard Gas Generator. It is envisioned that the results may suggest some minor changes in the unit, to be followed by another round of testing.

Assuming satisfactory test results, a Functional Requirements document will be generated to enable a Request for a Proposal to be issued to build a prototype unit by an ouside contractor. The prototype has to have a vacuum enclosure with a miniature ion pump and a battery power supply.

VII REFERENCES

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(3) "A Miniature Focal Plane Mass Spectrometer for Air Quality Measurement in Space Human Habitats", Mahadeva P. Sinha, SAE Technical Paper 981565, presented at the 28th International Conference on Environmental Systems, Danvers, MA, July 13-16, 1998.

VIII FIGURES

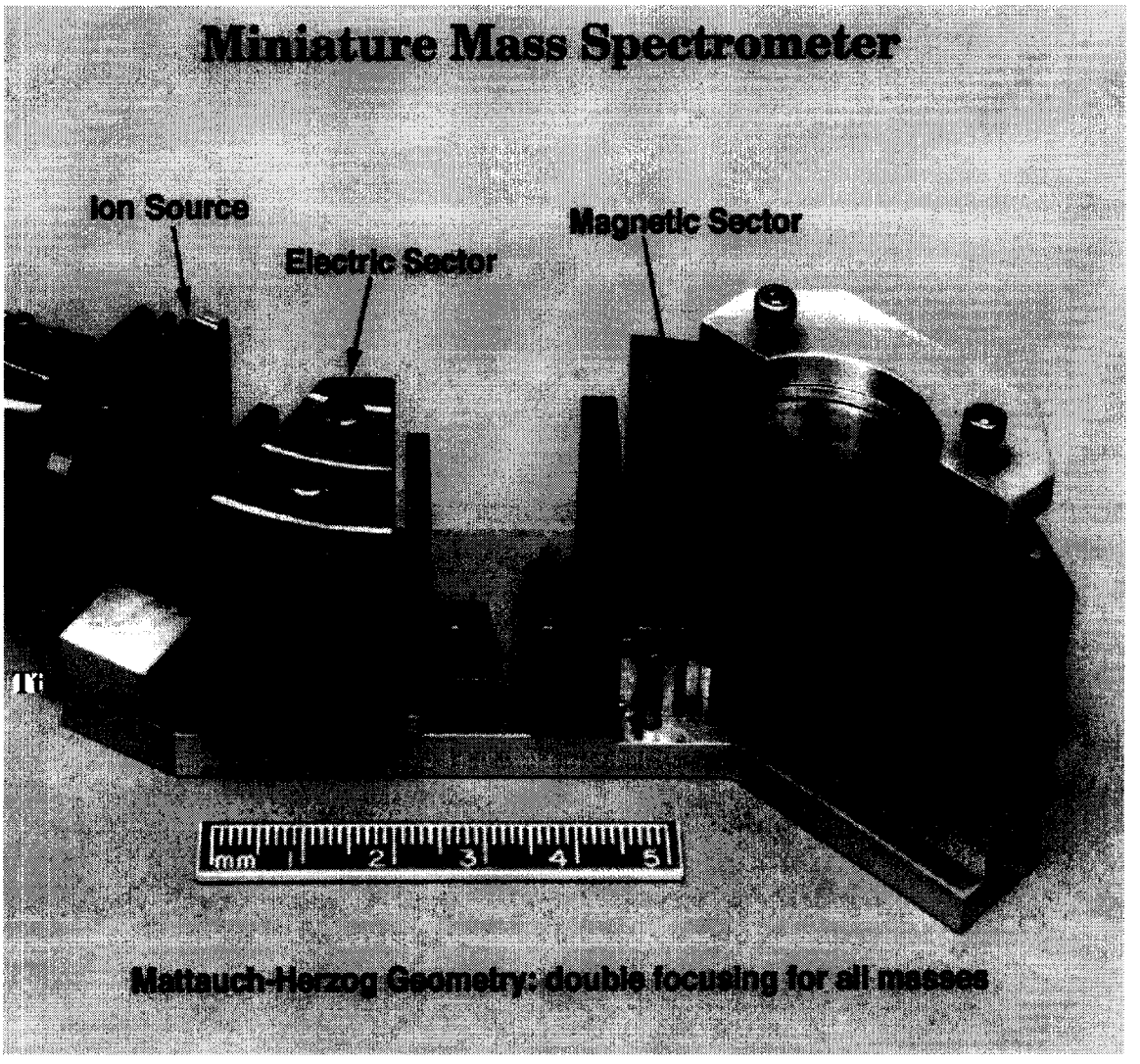

Figure 1 Miniature Mass Spectrometer

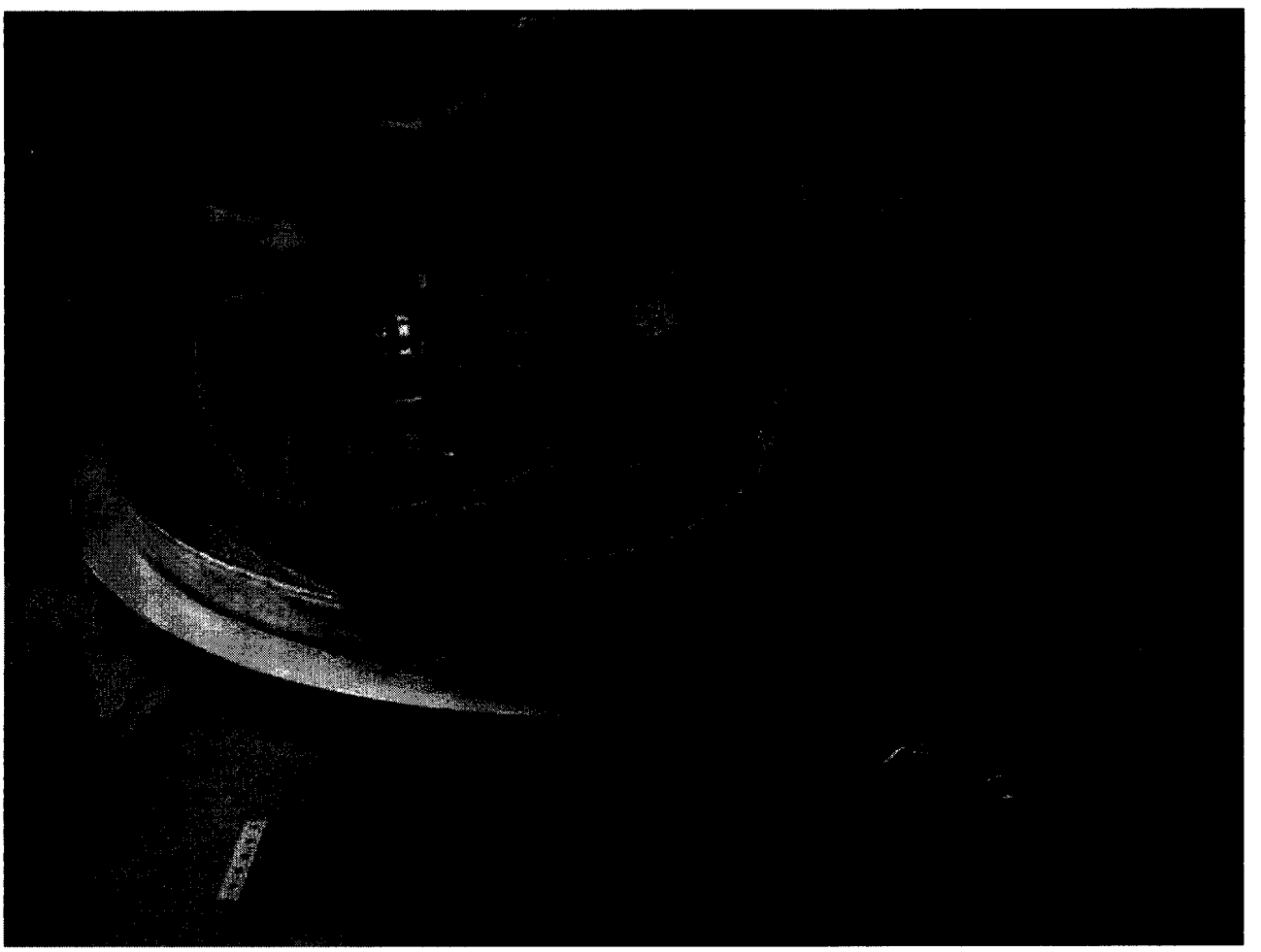

Figure 2 Miniature Mass Spectrometer operating in Bell Jar

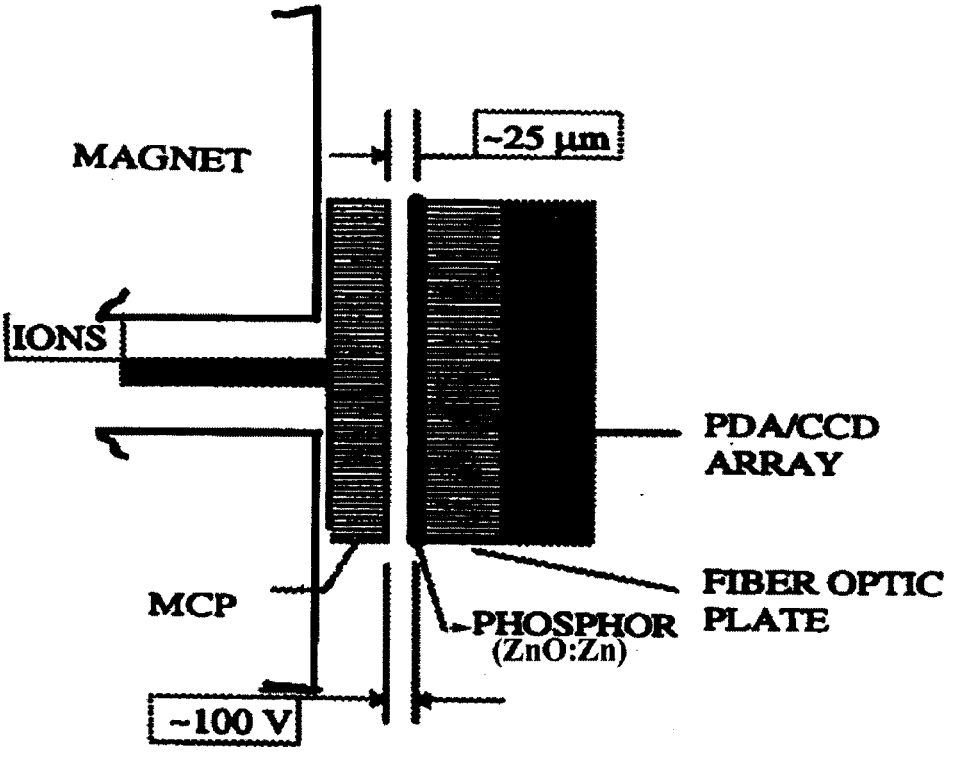

FIGURE 3 ELECTRO-OPTIC DETECTOR

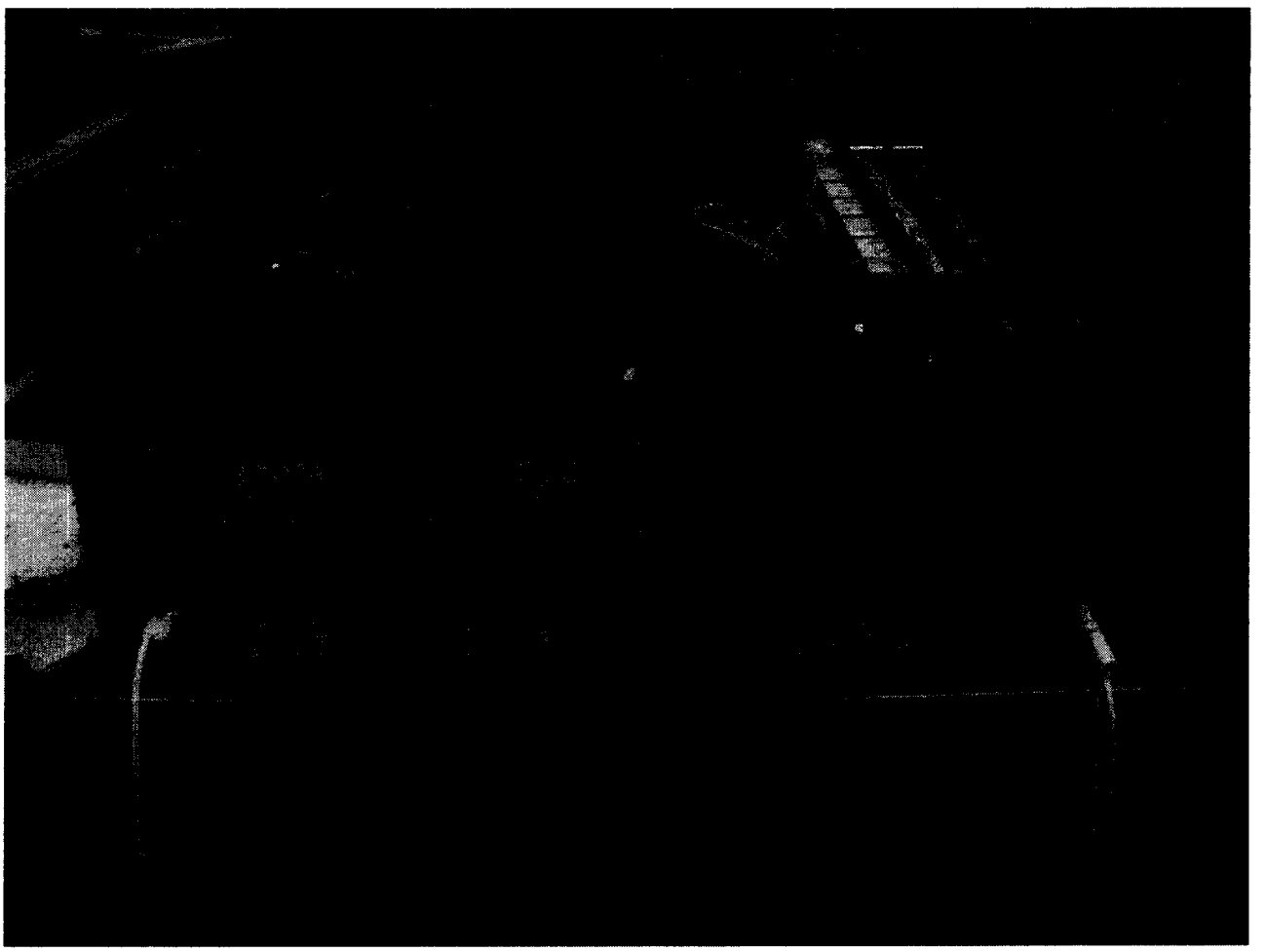

Figure 4 High Voltage Power Supply