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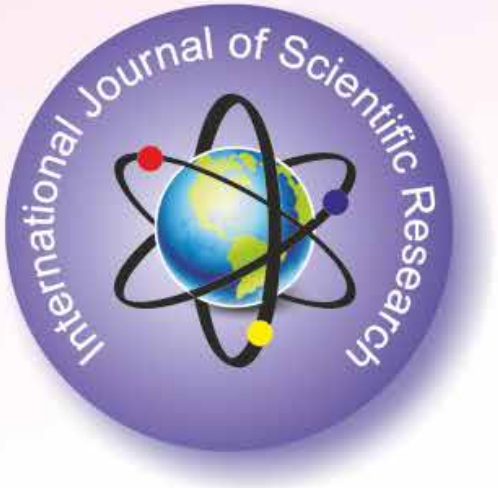


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Research Paper

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# Determination Of Inorganic Hazardous Air Pollutant Levels In Ambient Air Repairable Suspended Particulate Matter (P.m10) In And Around Tirupati, Chittoor District, Andhra Pradesh, India.

CHEMISTRY

KEYWORDS :Tirupati – AAQ- Inorganic Hazardous Air Pollutants (As, Ni, Se, Be, Cd, Cr, Co, Pb, Mn and Hg) – ICP-MS.

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## ABSTRACT

Air Pollution monitoring studies are one of the most important concern in this present environmental conditions of the atmosphere. Due to the industrialization, vehicular growing, urbanization day by day the air pollution levels are increasing rapidly. Today the air quality is quite different in urban areas and cities then compared too few years back of the natural air quality. USEPA has identified 188 compounds are hazardous depending upon its chemical and physical characteristics. These compounds are called as Hazardous Air Pollutants (HAPs). Out of these 188 compounds 33 compounds are most commonly found in urban areas. These pollutants will be generated from Industrial sources, vehicular emissions, burning of fossil fuels, etc.In this study we made an attempt to study the inorganic hazardous air pollutants like Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Mercury, Nickel and Selenium in Ambient Air Suspended Particulate Matter of in and around the Tirupati area. For this study we were selected five different sampling locations in Tirupati. Sampling was carried out 24 hourly and twice a week for P.M.10 in the month of February 2012. These samples were digested and subjected to analysis for As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg using Inductively Coupled Plasma -Mass Spectrometer (ICP-MS) based on USEPA Compendium method IO 3.5.The concentration levels of this inorganic hazardous air pollutant are summarized in Table-3 and Table-4.

### 1. Introduction

Ambient Air Quality evaluation studies are one of the most important concerns in these present environmental sconditions of the atmosphere. While compared to past decade, now a days the population increased, industrialization increased more than ten times, vehicular movement is also increased in cities and urban areas. Rapid growing of this Industrialization, utilization of fossil fuel for various industrial activities, vehicular movements and other man made sources; the pollution rate is increasing rapidly in the cities and urban areas. USEPA has identified 188 hazardous air pollutants which are called as HAPs. Out of these 33 HAPs are commonly identified in most of urban and cities. Particulate matter (PM) is linked with all sorts of health problems from a runny nose and coughing, to bronchitis, emphysema, asthma, and even death. Toxic (heavy) metals, chromium and nickel in particular, have been defined by the International Agency for Research on Cancer (IARC) as potential cancer causing agents1. Particles are generated to the atmosphere through a variety of physical and chemical mechanisms; these are emitted into the atmosphere from various sources, vehicular emission, industrial and natural processes, by combustion of fossil fuels etc. In ambient air, metals, metalloids and their compounds are mainly encountered as part of particulate matter. They may be present in the non-soluble, non-stoichiometric mixture phase (for example as spinels) or as soluble ionic compounds (salts). To a lesser extent and under certain Environmental conditions, gaseous forms (e.g. organometallic compounds) occur which may or may not be adsorbed on particles.The effects of toxic air pollutants in particulate matters on environment and human health have been of great global concern. Atmospheric toxic air pollutants are found in urban areas represent a mixture of primary particles emitted from various sources and secondary particles from aerosols formed by chemical reactions. The morphology and composition of these particles may change through several processes, including vapour condensation, evaporation and coagulation. The final 'products' usually vary according to origin, chemical composition and physical properties, leading to particular deposition patterns in the human respiratory system. The high influx of population to urban areas, increase in consumption patterns and unplanned urban and industrial development has led to the problem of air pollution.

### 2. Present Study

Tirupati is on of the famous pilgrim in Andhra Pradesh, India. Lakhs of pilgrims will visit Tirupati every day. The vehicular pollution is one of most important concern in Tirupati due to the pilgrim area. In view of the air pollution effects on human health, we made an attempt to study the levels of trace metals like As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg. USEPA has identified 188 compounds are hazardous air pollutants. As per USEPA Clean air Act -1970 the above specified eleven trace metals are called as Hazardous air pollutants. These pollutants may cause the health effects to human being and some of these metals are also may cause cancer to the human body. Some of these hazardous air pollutants also give effect on future generations. The prime objective of the air monitoring is to evaluate the existing air quality of the Tirupati area with respect to these specified hazardous air pollutants (As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg) levels. For this study we selected five sampling locations which are having more vehicle moment. Ambient air quality monitoring has been carried out with a frequency of alternative days in week at each location. At each of these locations, sampling stations were operated for 24 hours. In this regard we collected fifteen RSPM (PM10) samples in five selected locations. These samples are collected both working days and holidays period in the month of February 2012. Ambient Air Particles with an aerodynamic diameter smaller than 10 µm (PM10) were collected on 8'x10' cellulose membrane filters exposed for 24 hours using Repairable Dust Samplers (Envirotech), at the average flow rate of 1.2 m3 /min. Filters were pre-weighed and then dried in a desiccators for at least 24 hours after being exposed to air. The samples are collected at the following locations in and around the Tirupati area:

- **Near S.V.U.Red Building**
- **Gandhi Road**
- **Near RTC Bus stand**
- **K.T.Road**
- **Alipiri Bypass road**

The details of sampling locations with date and time and total volume of air collected is given in below table.

**TABLE–1**
**DETAILS OF AMBIENT AIR QUALITY MONITORING LOCA-**

**TIONS**

| Sample Code | Location | Date and Time of Sampling Started | Date and Time of Sampling Started | Volume of Air Sampled |
|---|---|---|---|---|
| AAQ1 | Near S.V.U.Red Building | 05-02-2012 & 8:30 a.m | 06-02-2012 & 8:45 a.m | 1710 |
| AAQ2 | Near S.V.U.Red Building | 08-02-2012 & 7:30 a.m | 09-02-2012 & 8:00 a.m | 1648 |
| AAQ3 | Near S.V.U.Red Building | 10-02-2012 & 7:10 a.m | 11-02-2012 & 7:40 a.m | 1654 |
| AAQ4 | Gandhi Road | 05-02-2012 & 9:15 a.m | 06-02-2012 & 9:10 a.m | 1702 |
| AAQ5 | Gandhi Road | 08-02-2012 & 8:10 a.m | 09-02-2012 & 8:25 a.m | 1664 |
| AAQ6 | Gandhi Road | 10-02-2012 & 7:40 a.m | 11-02-2012 & 7:58 a.m | 1612 |
| AAQ7 | Near RTC Bus stand | 05-02-2012 & 8:35 a.m | 06-02-2012 & 8:52 a.m | 1714 |
| AAQ8 | Near RTC Bus stand | 08-02-2012 & 8:30 a.m | 09-02-2012 & 8:15 a.m | 1672 |
| AAQ9 | Near RTC Bus stand | 10-02-2012 & 8:15 a.m | 11-02-2012 & 8:32 a.m | 1646 |
| AAQ10 | K.T.Road | 05-02-2012 & 8:50 a.m | 06-02-2012 & 8:40 a.m | 1622 |
| AAQ11 | K.T.Road | 08-02-2012 & 8:45 a.m | 09-02-2012 & 9:05 a.m | 1648 |
| AAQ12 | K.T.Road | 10-02-2012 & 8:10 a.m | 11-02-2012 & 8:18 a.m | 1622 |
| AAQ13 | Alipiri Bypass road | 05-02-2012 & 9:40 a.m | 06-02-2012 & 9:30 a.m | 1650 |
| AAQ14 | Alipiri Bypass road | 08-02-2012 & 8:35 a.m | 09-02-2012 & 8:45 a.m | 1648 |
| AAQ15 | Alipiri Bypass road | 10-02-2012 & 8:05 a.m | 11-02-2012 & 8:20 a.m | 1636 |

**TABLE-2**
**TECHNIQUES USED FOR AMBIENT AIR QUALITY MONITORING**

| Sr. No. | Parameter | Technique | Technical Protocol | Minimum Detectable Limit (mg/m3) |
|---|---|---|---|---|
| 1 | As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg | ICP-MS | Based On USEPA Compendium Method IO – 3.5S | 0.001 |

**3. Analytical Methodology**

All the filter papers has coded and subjected to go for metal digestion and analysis of trace and toxic metals as per USEPA Compendium method -3.5. The PM10 filter paper is divided into 1 x 8 " strip equalling parts from the exposed filter. A part of filter strip is cut as small pieces and placed in an extraction tube. To this extraction tube 20 ml of the 4% Nitric acid is added and subjected to metal digestion.The extraction tube is closed with Cap and sonicated for 3 hours at 69 °C in sonication bath. The filter was occasionally checked during sonication period and used a clean pyrex or quartz glass rod to adjust the filter to the bottom of the tube without getting any floats out of the acid. After sonication, the sample is allowed to cool to room temperature and is filtered using Watman numbered 42 filter paper. The final volume of the sample is made up to 50 ml in volumetric flask with double distilled water. Transferred the sample extract to a polypropylene bottle then the sample was ready for analysis.In order to eliminate the interference from the filter paper, a blank sample treated and analyzed exactly in a similar way as that of sample filter paper. Inductively Coupled Plasma –Mass Spectrometer (ICP-MS) is one of the best techniques for determination of metal concentrations up to ppb levels in different matrices. By using this ICP-MS we can able to determine the metal concentrations upto ng/m3 in Ambient Air Particulate matters. Multi elements standard was used to determine all the eleven metal concentrations in single aspiration. Seven different working standards were prepared and made standard curve using the standards in ICP-MS. The correlation coefficient is observed greater than 0.999 for each of the element. After the completion of standard curve preparation, one standard check and one QC check was analyzed. Seven different linear concentration standards were prepared, ranging from 0.001 mg/L–0.1 mg/L. Before conducting sample analysis, different concentrations of standards were analysed and linear curve was prepared. All metals having good linear graph with correlation coefficients of > 0.999 were observed in the preparation of standard curves.

**4. Results and Discussion:**

ICP-MS is the most useful technique for the determination of trace metals upto parts per trillion levels. Since, AAS-GFA is a single element analyser, it takes more time to analyse multiple elements. ICP-MS is a very useful technique to determine trace levels of metals in a single aspiration. In this study the following elements like As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg are analyzed in ambient air quality levels of Tirupati by using ICP-MS techniques. The test results are shown in Table-1 and Table -2.

**Table -1**
**Test Results of Hazardous Air Pollutants (Inorganic) in and Around the Tirupati**

| Sample Code | Location | Date of Sampling | Arsenic as As | Lead as Pb | Beryllium as Be | Cadmium as Cd | Chromium as Cr | Manganese as Mn |
|---|---|---|---|---|---|---|---|---|
| Unit | - | - | ng/m3 | µg/m3 | ng/m3 | ng/m3 | µg/m3 | µg/m3 |
| AAQ1 | Near S.V.U. Red Building | 02-02-2012 | 3.4 | 0.13 | 10.3 | 5.4 | 0.041 | 0.34 |
| AAQ2 | Near S.V.U. Red Building | 04-02-2012 | 3.2 | 0.11 | 14.2 | 7.2 | 0.036 | 0.23 |
| AAQ3 | Near S.V.U. Red Building | 06-02-2012 | 3.2 | 0.086 | 13.8 | 5.8 | 0.022 | 0.29 |
| AAQ4 | Gandhi Road | 02-02-2012 | 2.8 | 0.19 | 10.4 | 6.9 | 0.029 | 0.19 |
| AAQ5 | Gandhi Road | 04-02-2012 | 2.9 | 0.22 | 11.9 | 4.9 | 0.024 | 0.24 |
| AAQ6 | Gandhi Road | 06-02-2012 | 3.4 | 0.26 | 8.6 | 4.1 | 0.018 | 0.22 |
| AAQ7 | Near RTC Bus stand | 02-02-2012 | 3.8 | 0.49 | 9.2 | 12.1 | 0.048 | 0.37 |
| AAQ8 | Near RTC Bus stand | 04-02-2012 | 4.4 | 0.42 | 14.3 | 10.7 | 0.044 | 0.41 |

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|---|---|---|---|---|---|---|---|---|
| AAQ9 | Near RTC Bus stand | 06-02-2012 | 4.0 | 0.44 | 12.1 | 9.7 | 0.047 | 0.38 |
| AAQ10 | K.T.Road | 02-02-2012 | 3.1 | 0.39 | 8.8 | 8.8 | 0.029 | 0.27 |
| AAQ11 | K.T.Road | 04-02-2012 | 2.2 | 0.28 | 11.9 | 7.9 | 0.036 | 0.22 |
| AAQ12 | K.T.Road | 06-02-2012 | 2.9 | 0.41 | 13.4 | 8.4 | 0.040 | 0.42 |
| AAQ13 | Alipiri Bypass road | 02-02-2012 | 2.8 | 0.40 | 9.8 | 7.9 | 0.029 | 0.32 |
| AAQ14 | Alipiri Bypass road | 04-02-2012 | 3.8 | 0.37 | 12.8 | 8.8 | 0.028 | 0.23 |
| AAQ15 | Alipiri Bypass road | 06-02-2012 | 3.4 | 0.40 | 13.6 | 4.9 | 0.034 | 0.31 |

**Table -2**
**Test Results of Hazardous Air Pollutants (Inorganic) in and Around the Tirupati**

| Sample Code | Location | Date of Sampling | Selenium as Se | Antimony as Sb | Cobalt as Co | Mercury as Hg |
|---|---|---|---|---|---|---|
| Unit | - | - | ng/m3 | ng/m3 | ng/m3 | ng/m3 |
| AAQ1 | Near S.V.U. Red building | 02-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ2 | Near S.V.U. Red building | 04-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ3 | Near S.V.U. Red building | 06-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ4 | Gandhi Road | 02-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ5 | Gandhi Road | 04-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ6 | Gandhi Road | 06-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ7 | Near RTC Bus stand | 02-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ8 | Near RTC Bus stand | 04-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ9 | Near RTC Bus stand | 06-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ10 | K.T.Road | 02-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ11 | K.T.Road | 04-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ12 | K.T.Road | 06-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ13 | Alipiri Bypass road | 02-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ14 | Alipiri Bypass road | 04-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |
| AAQ15 | Alipiri Bypass road | 06-02-2012 | <1.0 | <1.0 | <1.0 | <1.0 |

**4.1. Discussion:**
Selenium, Antimony, Cobalt and Mercury are found Below Detection Limit (i.e -<1 ng/m3).

**4.2. Arsenic:**
The arsenic levels in ambient air quality of in and around the Tirupati area is ranging from 2.2 – 4.4 ng/m3. The higher concentration of arsenic is observed in near RTC bus stand area and lower concentration level of arsenic is observed in K.T.Road.

**4.3. Lead:**
The Lead levels in ambient air quality of in and around the Tirupati area is ranging from 0.086 – 0.49 µg/m3. The higher concentration of Lead is observed in near RTC bus stand area and lower concentration level of lead is observed in near S.V.U.Red Building.

**4.4. Cadmium:**
The Cadmium levels in ambient air quality of in and around the Tirupati area is ranging from 4.1 – 12.1 ng/m3. The higher concentration of Cadmium is observed in near RTC bus stand area and lower concentration level of lead is observed in Gandhi Road.

**4.5. Beryllium:**
The Beryllium levels in ambient air quality of in and around the Tirupati area is ranging from 8.6 – 14.3 ng/m3. The higher concentration of Beryllium is observed in near RTC bus stand area and lower concentration level of lead is observed in Gandhi Road.

**4.6. Chromium:**
The Chromium levels in ambient air quality of in and around the Tirupati area is ranging from 0.018 – 0.048 µg/m3. The higher concentration of Chromium is observed in near RTC bus stand area and lower concentration level of lead is observed in near Gandhi Road.

**4.7. Manganese:**
The Manganese levels in ambient air quality of in and around the Tirupati area is ranging from 0.19 – 0.42 µg/m3. The higher concentration of Chromium is observed in KT Road area and lower concentration level of lead is observed in near Gandhi Road.

**5. CONCLUSION:**
In this study eleven Inorganic Hazardous Pollutants like As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg are studied in ambient air quality levels of in and around the Tirupati area. In this study Se, Co, Sb and Hg are observed Below Detection Limit (i.e 1.0 ng/m3). The concentration levels of As, Ni and Pb in Ambient Air Quality of Tirupati area is less than that of NAAQS amended on 16th November 2009, published by Ministry of Environment and Forestry, Govt.of India. Mn, Be, Cd and Cr pollutants are detected in the ambient air quality of Tirupati area, but there is no specified limits for these pollutants. However, this study has given an awareness of concentration levels of Inorganic Hazardous Air Pollutants like As, Be, Cd, Cr, Co, Ni, Mn, Pb, Se and Hg in Ambient air Quality of Tirupati.

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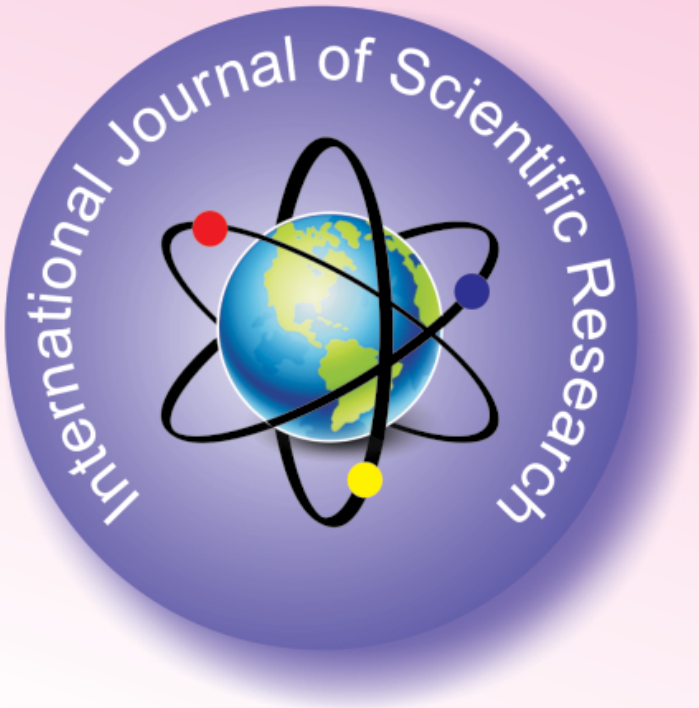


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