Air Pollution and EPR

Outdoor air pollution is a major environmental hazard that affects the health of people worldwide. The link between inhalation of ambient particulate matter (PM) and various adverse health effects is documented extensively by epidemiological and toxicological studies:

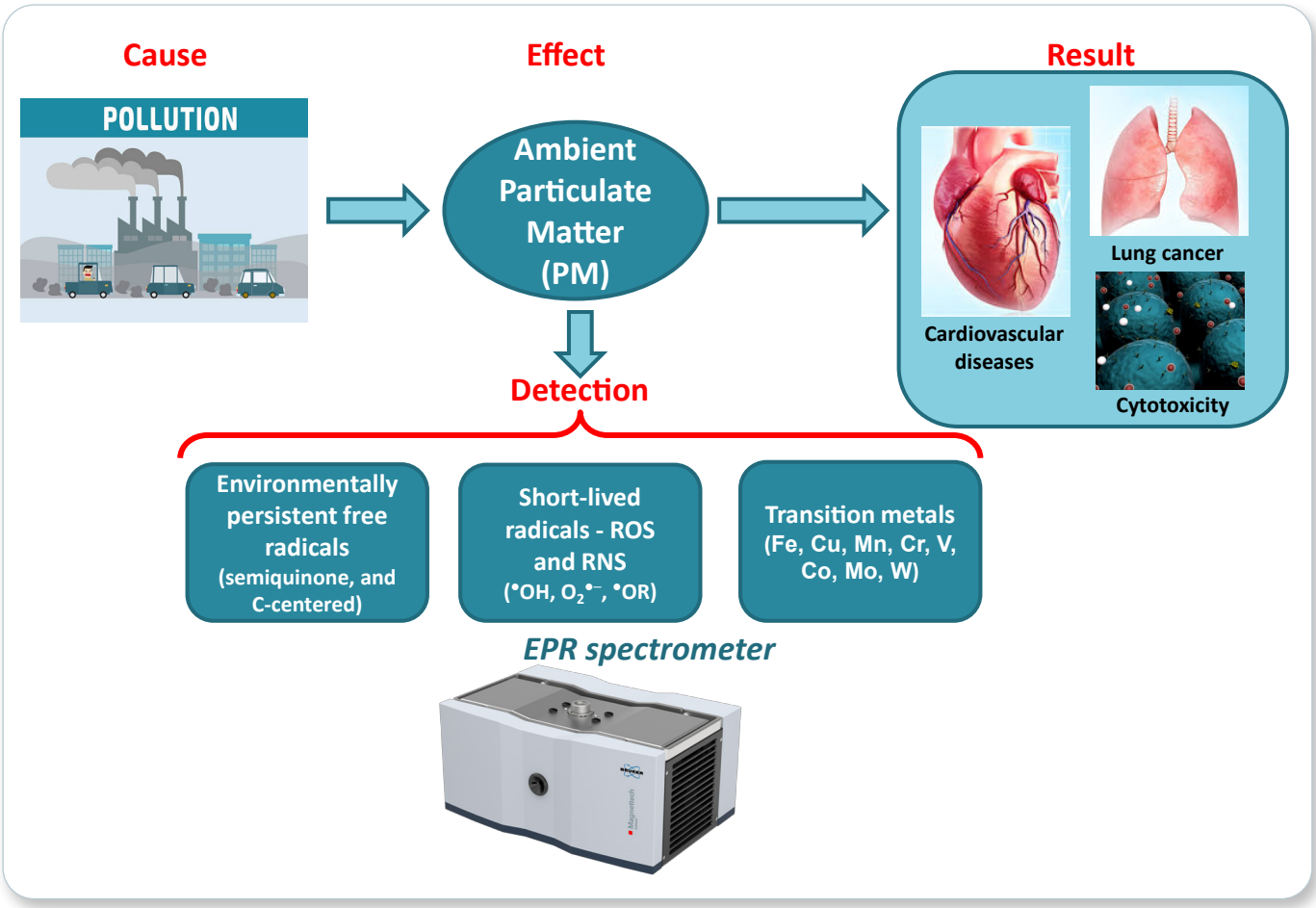
- Transition metals (Fe, Cu, Mn, Cr, V, Co, Mo, W) are identified as crucial PM components triggering hydroxyl radical (•OH) generation via Fenton-like reactions. This shows that the oxidative potential of PM is an important health-relevant metric.
- Reactive oxygen and nitrogen radical species (ROS and RNS) are produced from polycyclic aromatic hydrocarbons (PAHs) and redox cycling quinoids that are part of PM. These short-lived toxic radicals have tremendous potential for harmful oxidative effects in pulmonary tissue.
- Long-lived radicals, called environmentally persistent free radicals (EPFRs), are also part of ambient PM. They are typically oxygen-centered semiquinone or carbon-centered PAH radicals that promote the generation of ROS. Their half-life varies from several days to several months and even indefinitely on the internal surface of fine particles.

Electron Paramagnetic Resonance (EPR) spectroscopy is the only technique for the direct and non-invasive detection of transition metals and free radicals. By analyzing an EPR signal, one can identify, quantify and monitor intrinsic generation of short-lived (ROS and RNS) and long-lived (EPFRs) radicals from ambient particulate matter. EPR is capable to detect traces of transition metals down to parts per billion levels.

Challenge: Identifying and monitoring generation of free radicals from ambient particulate matter and determining their oxidative potential is of great concern due to adverse effects on human health.

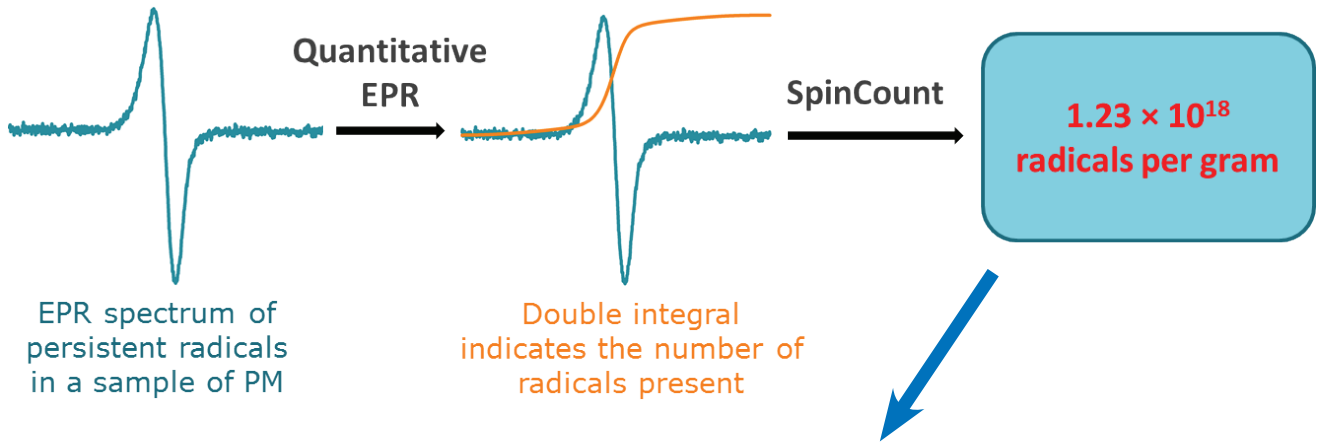
Solution: The Magnettech ESR5000 benchtop EPR spectrometer package

- Detects, identifies, and quantifies ROS, PAHs, EPFRs, and transition metals involved in the particulate matter chemistry
- Determines the oxidative potential of PM which is an important metric to estimate potential adverse effects
- Monitors radical reactions for better understanding of the oxidation mechanisms and to determine the half-life of the radicals



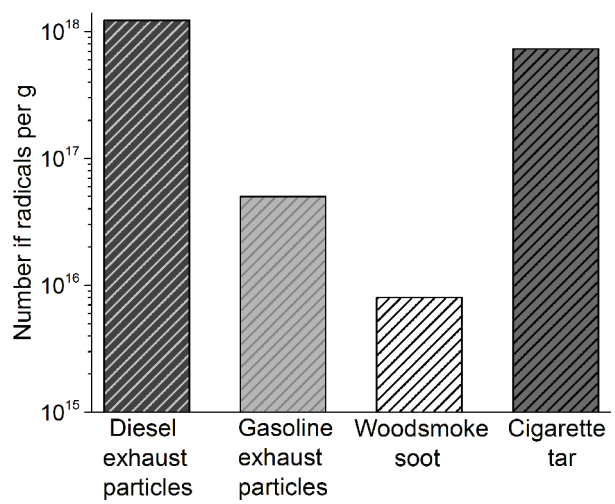
Magnettech ESR5000 key features:

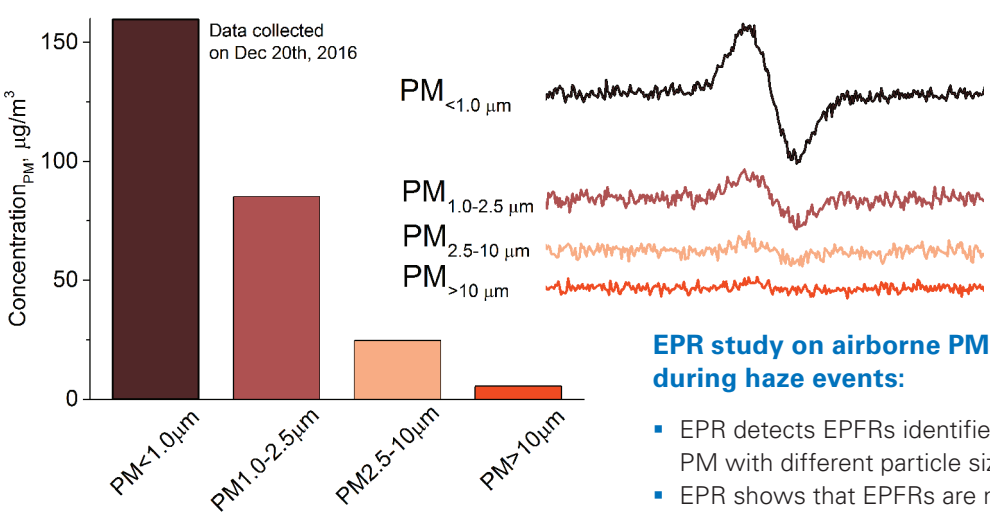
- No prior EPR experience needed
- Accurate results
- Superior sensitivity
- Ease of use
- Full workflow for measuring, analyzing and quantifying free radicals and transition metals
- Compact foot print
- Low cost of ownership



EPR analysis of PM from various air pollution sources

- EPR identifies and quantifies long-lived radicals, termed environmentally persistent free radicals (EPFRs).
- Depending on the EPR spectrum characteristics (g-factor) EPFRs are identified as O-centered semiquinone or C-centered PAH radicals.

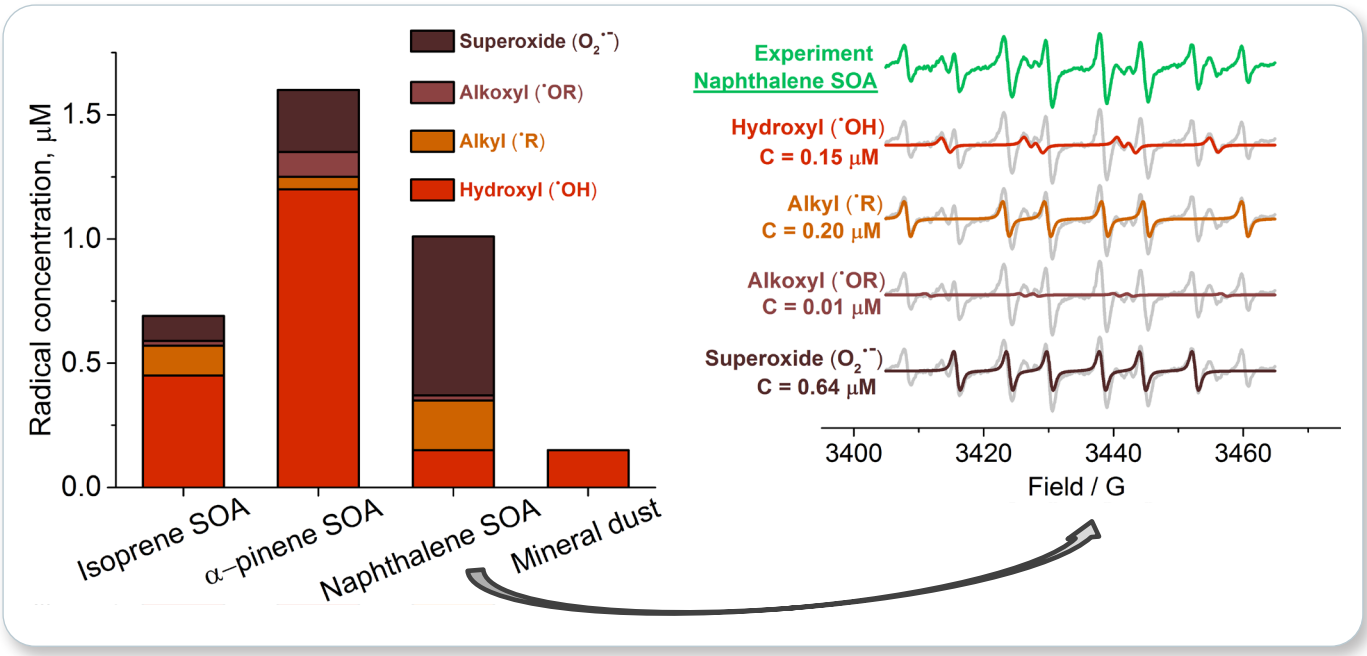




EPR study on airborne PM in Beijing during haze events:

- EPR detects EPFRs identified as semiquinone radicals in PM with different particle size.
- EPR shows that EPFRs are mainly persistent in the PM fraction of d_{ae} < 1 µm which are the most hazardous.
- The daily monitoring of the EPFRs (spins/g) shows environmental changes that impact long-term effects on human health.
- Such monitoring can be used to enact counter measures to reduce health risks to the public.

Analysis of radical content in PM



Mineral dust and secondary organic aerosols (SOA) account for major fraction of atmospheric PM:

- EPR detects toxic oxygen- and carbon-centered radical species in aqueous mixtures of SOA and mineral dust
- The radical formation is due to decomposition of organic hydroperoxides (ROOH) via homolytic cleavage or Fenton-like reactions:

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$
$$ROOH + Fe^{2+} \rightarrow RO^{\bullet} + {}^{-}OH + Fe^{3+}$$
$$ROOH + Fe^{2+} \rightarrow RO^{-} + {}^{\bullet}OH + Fe^{3+}$$

- EPR monitors, identifies, and quantifies different types of radicals that cause oxidative stress to lung cells and tissues.

Summary:

Detection, characterization, and monitoring of the free radical chemistry is essential and mandatory due to the adverse health effects of PM. The Magnettech ESR5000 is the solution to investigate and evaluate this important chemistry. With EPR you gain insight into the mechanisms generating significant amounts of toxic radicals from inhalable ambient particulate matter.

Furthur Reading

1. Tong H. et al., Reactive oxygen species formed in aqueous mixtures of secondary organic aerosols and mineral dust influencing cloud chemistry and public health in the Anthropocene, Faraday Discuss. (2017) 200 251
2. Yang L. et al., Highly elevated levels and particle-size distributions of environmentally persistent free radicals in haze-associated atmosphere, Environ. Sci. Technol. (2017) 51 7936
3. Borrowman C.K. et al., Formation of environmentally persistent free radicals from the heterogeneous reaction of ozone and polycyclic aromatic compounds, Phys. Chem. Chem. Phys. (2016) 18 205
4. Hellack B. et al., Oxidative potential of particulate matter at a German motorway, Environ. Sci.: Processes Impacts (2015) 17 868
5. Yang A. et al., Spatial variation and land use regression modeling of the oxidative potential of fine particles, Environ. Health Perspect. (2015) 123 1187

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