

New analytical methods and old BEI lead to the risk to underestimate styrene occupational exposure

Research

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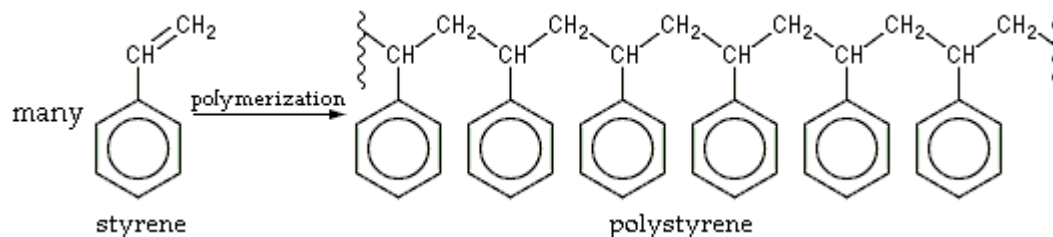
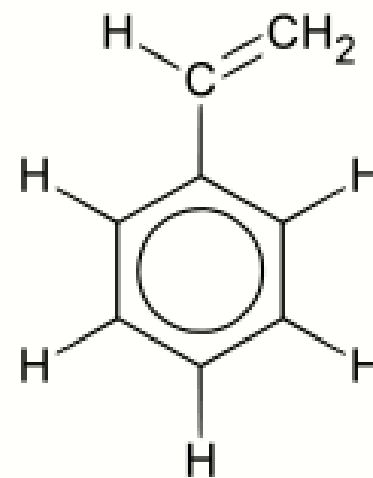
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Styrene Occupational Exposure

The evaporation of styrene from unsaturated polymeric resin into the work environment during processing in the Glass fibre-Reinforced Plastics (GRP) can result in workers' exposures to styrene.

Styrene toxicological properties are: short-term irritative effects, chronic effects on central nervous system, and an increased risk of leukemia and lymphoma.

IARC classified styrene as a Group 2B, possibly carcinogenic to humans.



Fiber-reinforced plastics



Fiber-reinforced plastics, also known as polymer composites, have been successfully used in many industrial, aerospace, automotive and military applications. Examples include bathtubs and shower stalls, hulls for recreational and commercial watercraft, power tools, automotive parts, and structural components for chemical process equipment and corrosion resistant storage tanks.



Open molding

With open molding, the gel coat and laminate are exposed to the atmosphere during the fabrication process. The **hand lay-up open molding process**, that involves 'layup' of several layers, either by hand or some type of mechanical application equipment, such as a spray gun. It is suitable for making a wide variety of composites products ranging from very small to very large.



Press Molding

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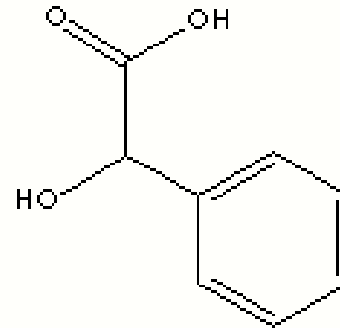
In closed molding, the composite is processed in a two-sided mold set, or within a vacuum bag.

In press molding, the mold set is mounted in a molding press and the molds are heated to 2500 to 4000 F.

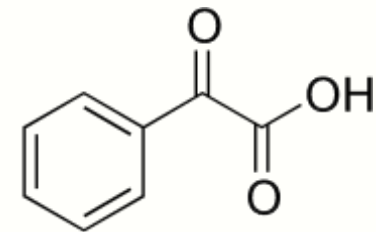


The ACGIH TLV® for styrene in the workplace air is **85 mg/m³** or 20 ppm.

The major metabolic pathway in humans is the oxidation to mandelic acid (MA) and further to phenylglyoxylic (PGA) acid, whose total concentration is the dose biomarker suggested by ACGIH for occupational exposure to styrene, with a BEI® of **400 mg/g of creatinine** in the end shift urine.



Mandelic acid



Phenylglyoxylic acid

The styrene exposure of 27 fiberglass workers was assessed by means of personal air monitoring (Radiello®) and by biological monitoring.

14 workers used the open molding and 13 the press molding technique.

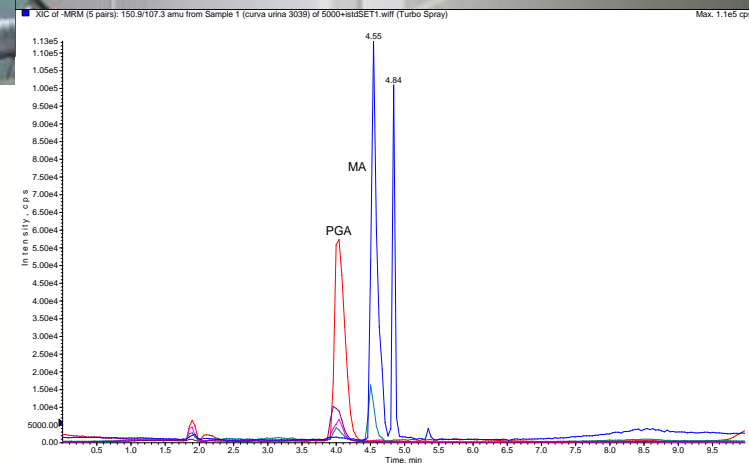


Biological monitoring method

Non occupational exposure to styrene is uncommon, but nevertheless MA + PGA are considered non specific biomarkers, as a background value is always found in human urine.

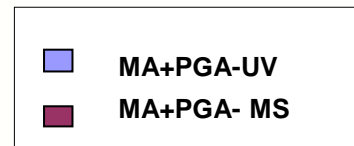
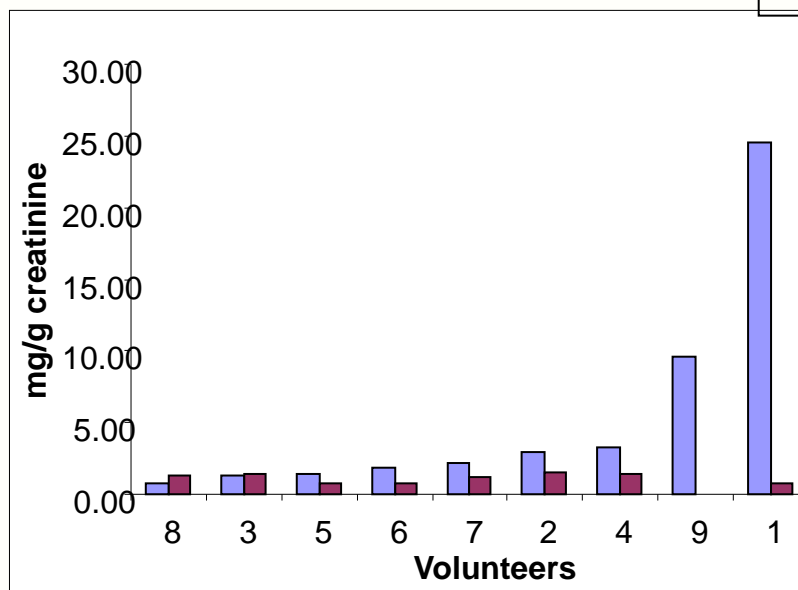
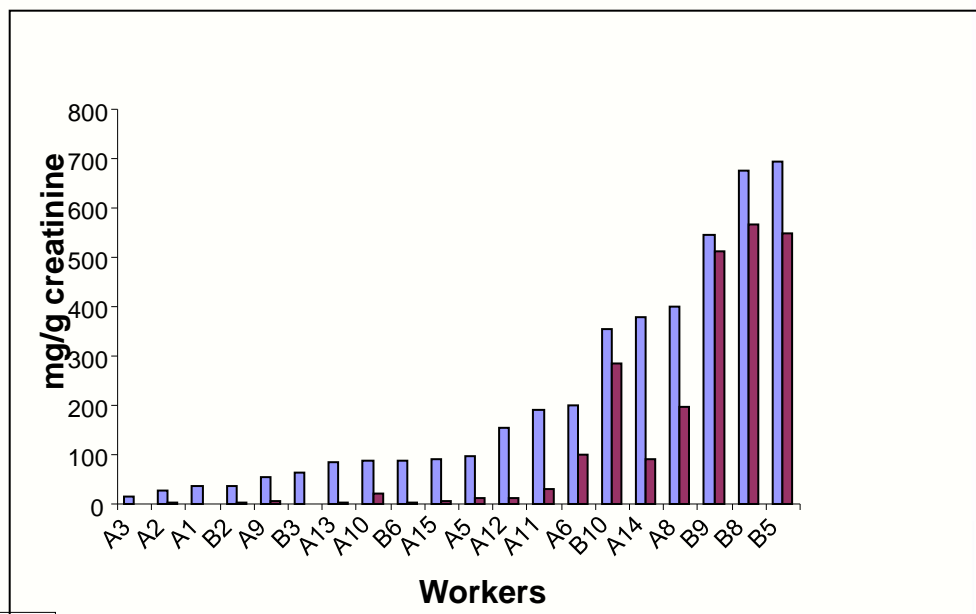
A review of the literature shows that most analytical methods applied to workers biomonitoring use HPLC-UV, a non specific analytical technique.

In this case the determination of urinary MA and PGA was performed by HPLC/MS/MS using the isotopic dilution method for quantitative analysis.



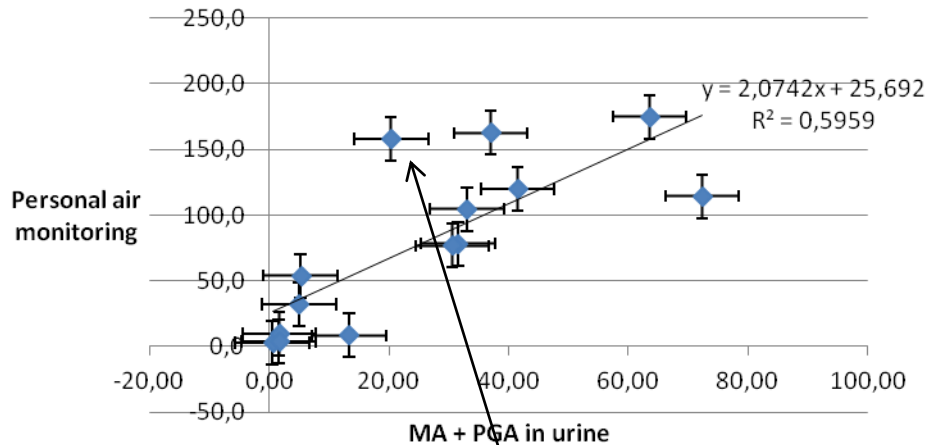
UV vs MS/MS detection

The urinary concentration of MA+PGA in 9 volunteers and 20 occupationally exposed workers measured using UV are significantly higher than those achieved with MS/MS, indicating that **UV detection overestimates the analyte concentrations, probably due to its poor specificity.**



Results

Open mold

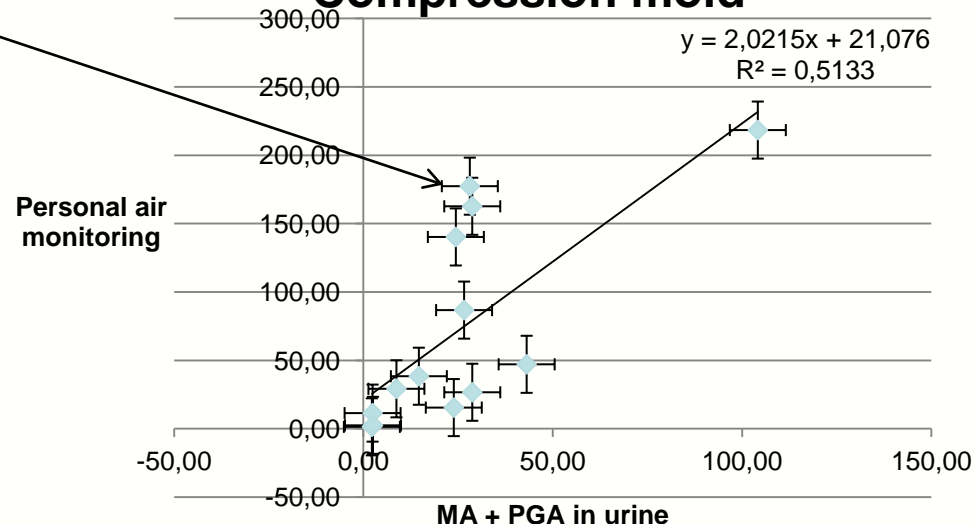


Results show that open molding involves, on average, a higher exposure level than compression molding, even if they appear to be below the ACGIH BEI ® of 400 mg/g creat.

For subjects having MA+PGA higher than expected, skin absorption can be hypothesized, even if a skin notation is not indicated by ACGIH. In fact the climatic conditions were characterized by high temperature and humidity. Literature data indicate that styrene damages human skin even at concentrations comparable to the TLV, and that oxidative stress is involved in these effects.

(C. Costa et al. / *Toxicology in Vitro* 20 (2006) 324–331).

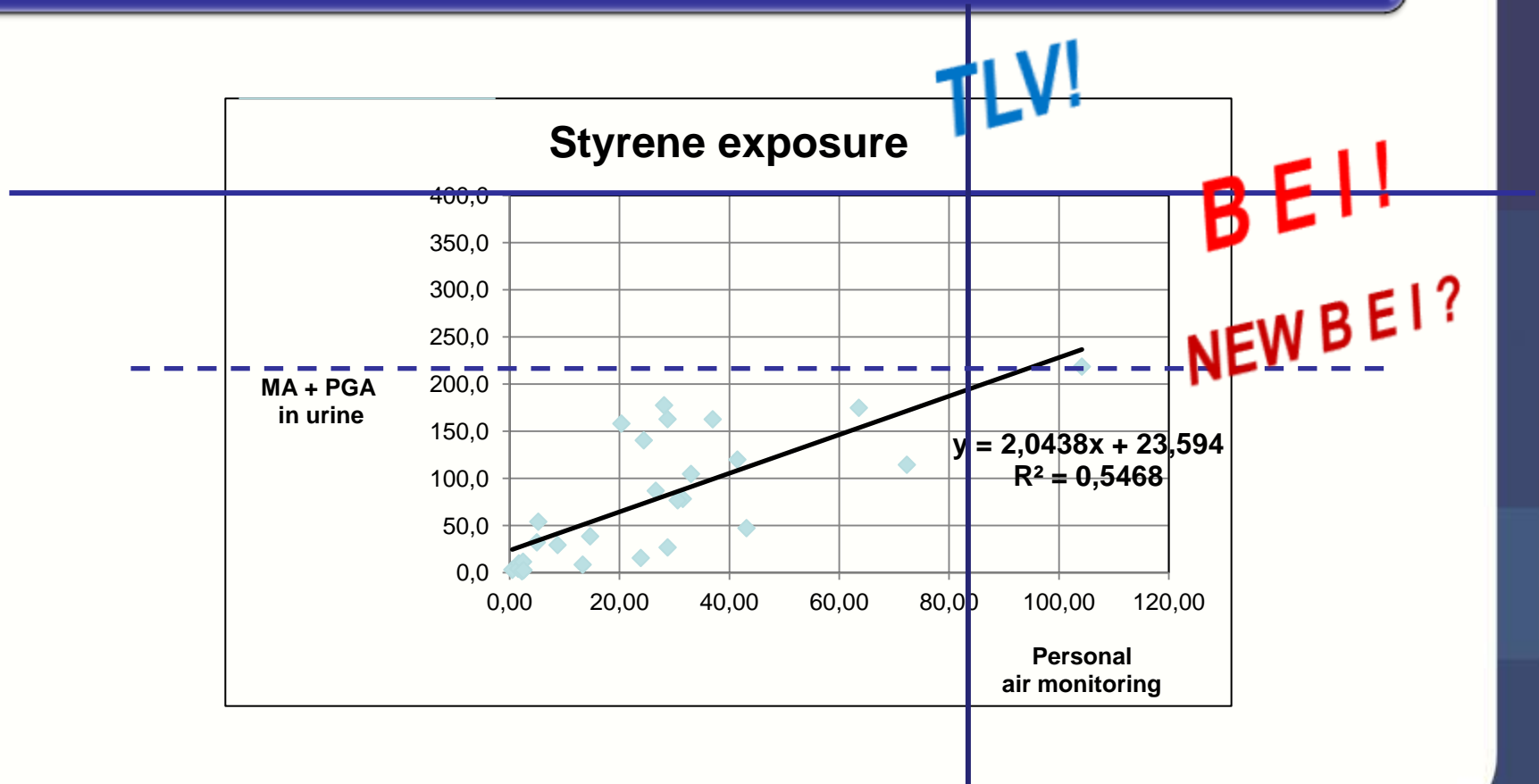
Compression mold



Results – all subjects

Pooling together all data, a good correlation is shown between personal air and biological monitoring ($R = 0.74$).

However, from the linear correlation equation, to a styrene value equal to TLV® (85 mg/mc) the corresponding MA+PGA value should be 197 mg/g of creatinine, while the BEI® is 400 mg/g of creatinine.



□ Press molding reduces the styrene exposures with respect to open molding but still we measure significant airborne styrene values, and personal and collective protection devices must be used.

□ Even if most literature data indicate that skin absorption for styrene is not important, climatic conditions, repeated exposures and damaged skin can increase its role.

□ New literature indicate that the skin of subjects occupationally exposed to organic solvents can be always considered a target of their toxicity; inobservance of safety rules and precautions during their use can lead to oxidative damage of the macromolecular constituents of the exposed subjects skin.

□ The use of new and highly specific analytical methods like HPLC with tandem mass spectrometry detection can lead to urinary metabolite levels more reliable but lower in value than those obtained with less specific techniques like HPLC with UV detection.

□ This is the case of MA and PGA, whose BEI have been set on the basis of HPLC UV results and therefore the comparison of HPLC/MS/MS results with the BEI value of 400 mg/g of creatinine in end shift urine leads to the risk to underestimate styrene exposure.

□ The collection of new results, obtained using highly specific and fully validated analytical methods for biological monitoring, is a research priority in order to revise Biological Limit Values.