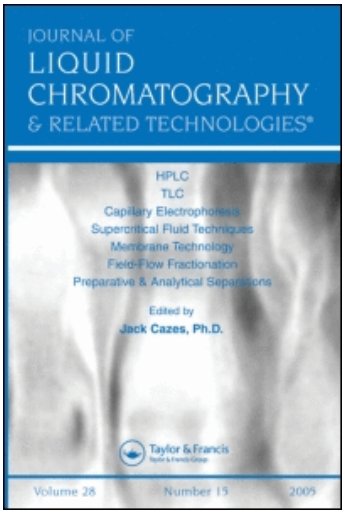


**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Determination of Dicyandiamide with Non-Aqueous Polar Eluent

Jari Pukkila[a]; Kimmo Peltonen[a]
[a] Institute of Occupational Health Topeliuksenkatu, Helsinki, Finland

**To cite this Article** Pukkila, Jari and Peltonen, Kimmo(1990) 'Determination of Dicyandiamide with Non-Aqueous Polar Eluent', Journal of Liquid Chromatography & Related Technologies, 13: 2, 409 — 414
**To link to this Article: DOI:** 10.1080/01483919008049553
**URL:** http://dx.doi.org/10.1080/01483919008049553

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(2), 409-414 (1990)

# DETERMINATION OF DICYANDIAMIDE WITH NON-AQUEOUS POLAR ELUENT

**JARI PUKKILA AND KIMMO PELTONEN**
*Institute of Occupational Health*
*Topeliuksenkatu 41 a A*
*00250 Helsinki, Finland*



## ABSTRACT

Epoxy powder paints are characterized by their dicyandiamide content. Dicyandiamide is determined on a amino bonded phase column with non-aqueous but polar eluent consisting of methanol and acetonitrile (5/95, v/v). The elution order of the components is that of normal phase but the eluent is more like reversed phase. This method is essentially faster than the previous methods in the analysis of dicyandiamide in multicomponent powder extracts.

## INTRODUCTION

Dicyandiamide or cyanguanidin is a widely used hardener in the thermal curing of epoxy resins. In powder painting, dicyandiamide is specifically used in epoxy powder coatings that produce a glossy finish. Unknown powder samples - samples from the air or from the folds of worker clothing - can therefore be differentiated in semiglossy or glossy types by the presence of dicyandiamide in them. It is the semiglossy type that is known to cause occupational health effects in case of repeated skin contact. Dicyandiamide is readily extractable from the coating powders with polar solvents.

RP-HPLC has been used in the determination of the highly polar dicyandiamide (DCDA). DCDA has been separated with plain distilled water (1,2), with water containing ion pairing reagents (3) or with acetonitrile modified eluents (4).

Extracts from uncured coating powders contain a large fraction of components less polar than DCDA. Separation in the reversed phase mode with the aforementioned water rich eluents would therefore be very time-consuming even if high gradients were used with an organic modifier. A new and faster method utilizing non-aqueous but polar eluents was developed. The new method utilizes a mixture of methanol and acetonitrile on a amino bonded phase column and provides with a fast DCDA analysis while maintaining full compatibily with polar extraction solvents.



## MATERIALS AND METHODS

### Chemicals

Epoxy resin based coating powders of the semiglossy type were obtained from leading manufacturers in Finland and were used as marketed containing all additives. 97 % pure dicyandiamide (EGA-Chemie, Steinheim, W-Germany) was used for the external standards. Methanol and acetonitrile were of HPLC grade and supplied by Lab-Scan Analytical Sciences.

### Sampling and Extraction

Air samples can be collected on 13 or 37 mm glass fibre filters (type AE, SKC-Inc, USA). Air sampling rate is typically 1.0 l/min. Filters are immersed in 1.0 ml of acetonitrile in a test

tube. Other samples, such as powders that are wiped from surfaces or from clothing can simply be placed in a test tube. The tubes are sonificated for one hour. Injections into HPLC can be made directly from the supernatant but some dilutions are usually necessary before injections. External standards are made in acetonitrile.

## Separation

HPLC separations were done on a Pye Unicam Model 100A liquid chromatograph equipped with a Rheodyne 7125 injector with a 20 µl loop and a Pye Unicam LC-XP gradient programmer was used together with a Pye Unicam UV photometric detector. The detector was operated at 220 nm.

The column was a Spherisorb $NH_2$ (5µ, 250x4.6 mm I.D., Phase Separations, UK). The mobile phase was a mixture of methanol and acetonitrile (1/99, v/v). The flow rate was 1.0 ml/min.



## RESULTS AND DISCUSSION

DCDA has a very low solubility in non-polar solvents. From the extraction point of view, polar solvents are preferred. Compatibility of the extraction solvents with HPLC eluents suggests the use of reversed phase mode in the analysis. A reversed phase liquid chromatographic separation of small and highly polar amines like dicyandiamide is, however, characterized with low retention. It may be the reason why in previous methods (1-3) plain water or buffered water were used as eluents with no organic modifier. Well separated DCDA peaks clearly resolved from the solvent peak were obtained though.

The retention behaviour reported in the previous papers could not, however, be repeated with our columns of the same

functionalities. DCDA simply elutes with the solvent peak. Reason for this is not understood by the authors. Nevertheless, with only one component in the eluent as in the water using methods, the retention of DCDA relative to the other possible components in the sample can not be adjusted. Even if sufficient separation with the previous methods were obtained for DCDA, the powder paint related DCDA analyses would be unnecessarily time-consuming since a powder extract always contains compounds that elute with much longer retention times under water rich conditions.

Liquid chromatographic conditions were searched that combine fast analysis with eluent compatibility and still provide with controllable retention times for DCDA. A binary mixture of methanol and acetonitrile was found to meet with the requirements if methanol content of the eluent is controlled and if an amino bonded phase column is used.

It is methanol that determines the DCDA retention in this method. Methanol content can be varied only within the range of 1-5%. Exceeding 5 % makes DCDA elute with the solvent peak. Likewise, introduction of salts like sodium perchlorate suppresses the retention completely.

Peak shapes are very sensitive to the solvent of the sample. Water samples of DCDA produce only badly deformed peaks. Acetonitrile is recommended as a solvent for the external standards and for the extraction of sample powders. The new method has a limit for DCDA retention beyond which the retention times can not be extended. The limit is reached at 0 % percent methanol in the eluent. The method is still very useful for DCDA determinations from powder paint matrixes since the totally organic mobile phase elute other components of the extract in one large peak before DCDA immediately after injection. DCDA is well separated from that peak (fig.1). Longer retention times might be obtained if less polar solvent was used as the main component of the eluent instead of

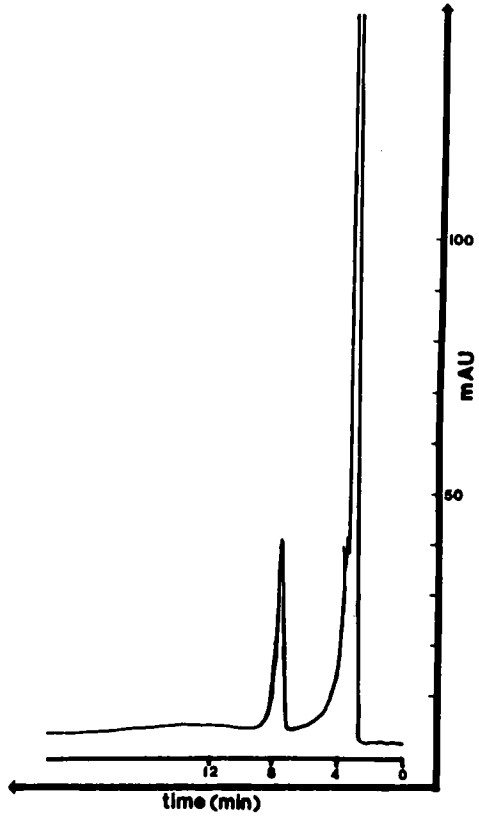


FIGURE 1. Powder (300µg) extract showing the separation of DCDA from the other components eluting together before DCDA.

acetonitrile. Miscibility and low UV cut off requirements limit the amount of possible solvents practically to acetonitrile only.

Experiments with Spherisorb columns of the same length but with packings of different functionalities were performed. No retention was obtained with the $ODS_2$ column. The cyano bonded phase column showed retention behaviour similar to the $NH_2$ but the peak shapes remained poor.

No more DCDA can be extracted from a powder sample after two extractions. Analyses revealed that glossy epoxy coating powder to

be thermally cured contain about 2 % DCDA. The detection limit for DCDA is about 20 ng/ml at the signal to noise ratio of 2. That means that theoretically 1 µg of powder is sufficient for powder characterization purposes. Powder samples from the air are usually on the mg range.

## ACKNOWLEDGEMENTS

Financial support from The Finnish Work Environmental Fund is gratefully acknowledged.



## REFERENCES

1. Burrows E.P., Brueggeman E.E., Hoke S.T., Chromatographic Trace Analysis of Guanidine, Substituted Guanidines and s-Triazines in Water, J. Chromatogr. 294, 494, (1984).

2. Hagnauer G.L., Dunn D.A., HPLC. A Reliable Technique for Epoxy Resin Prepreg Analysis, Ind. Eng. Chem. Prod. Res. Dev. 21, 68, (1982).

3. Vilsmeier K., Bestimmung von Dicyandiamid, Nitrit und Nitrat in Bodenextracten mit Hochdruckflussigkeitschromatographie, Z. Pflanzenernaehr. Bodenk. 147, 264, (1984).

4. Noel D., Cole K.C., Hechler J.J., High-Speed Reserve Phase Liquid Chromatography with 3µ Packing for Analysis of Fiber-Reinforced Epoxy Composite Formulations, J. Appl. Polym. Sci. 32, 3097, (1986).