

# Towards the use of DGT technique in a regulatory context for monitoring metals in marine water bodies : Results of an International Intercomparison Exercise

Gonzalez J. L.<sup>1</sup>, Amouroux I.<sup>2</sup>, Guesdon S.<sup>3</sup>, Menet-Nédélec F.<sup>4</sup>, Ponzevera E.<sup>2</sup>, Montero N.<sup>5</sup>, Rodríguez J. G.<sup>5</sup>, Belzunce-Segarra M. J.<sup>5</sup>, Larreta J.<sup>5</sup>, Menchaca I.<sup>5</sup>, Marras B.<sup>6</sup>, Schintu M.<sup>6</sup>, Caetano M.<sup>7</sup>, Correia Dos Santos M.<sup>8</sup>, Rodrigo Sanz M.<sup>9</sup>, Millán Gabet V.<sup>9</sup>, Bersuder P.<sup>10</sup>, Bolam T.<sup>10</sup>, Regan F.<sup>11</sup>, White B.<sup>11</sup>, Zhang H.<sup>12</sup>

IFREMER-France, <sup>1</sup>LITTORAL, F-83607 La Seyne/mer, <sup>2</sup>Unit of Biogeochemistry and Ecotoxicology, F-44980 Nantes, <sup>3</sup>LITTORAL, F-17390 La Tremblade, <sup>4</sup>LITTORAL, F-14620 Port-en-Bessin, <sup>5</sup>AZTI-Spain, 20110 Pasaia, <sup>6</sup>UNICA-Italy, 06124 Cagliari, <sup>7</sup>IPMA-Portugal, 1466-166 Algés, <sup>8</sup>IST-Portugal, 1046-001, Lisboa, <sup>9</sup>ITC-Spain, 36116 Sta. Lucía, Las Palmas, <sup>10</sup>CEFAS-United Kingdom, Lowestoft, Suffolk, NR33 0HT, <sup>11</sup>DCU-Ireland, Dublin 6, <sup>12</sup>Lancaster University-United Kingdom, Lancaster LA1 4YQ



## Objective

In order to move forward in the acceptance of a novel contaminant monitoring technique for the status assessment of marine water bodies, sensu the Water Framework Directive (WFD), an Inter-Laboratories Comparison (ILC) exercise was organized by Ifremer in the framework of the MONITOOL project - New tools for monitoring the chemical status in transitional and coastal waters under the EU WFD. This ILC focused on the use of DGT technique for the measurement of WFD priority metals (Cd, Ni and Pb).

The objectives of this ILC were to test the performance of laboratories when analysing DGTs and to identify the critical handling (resin gel retrieval and elution) and analytical steps when working with DGT samplers, to establish recommendations to prevent misleading results.

## Design of the ILC experiment

The experimental design consisted of the deployment by Ifremer of DGT samplers (DGT Research Ltd., Lancaster, UK) at a marine site (Lazaret Bay, France) and the subsequent delivery to participants of these DGTs and DGT components at various stages of handling and analysis, to enable a step-by-step investigation of where biases are introduced (Figure 1).

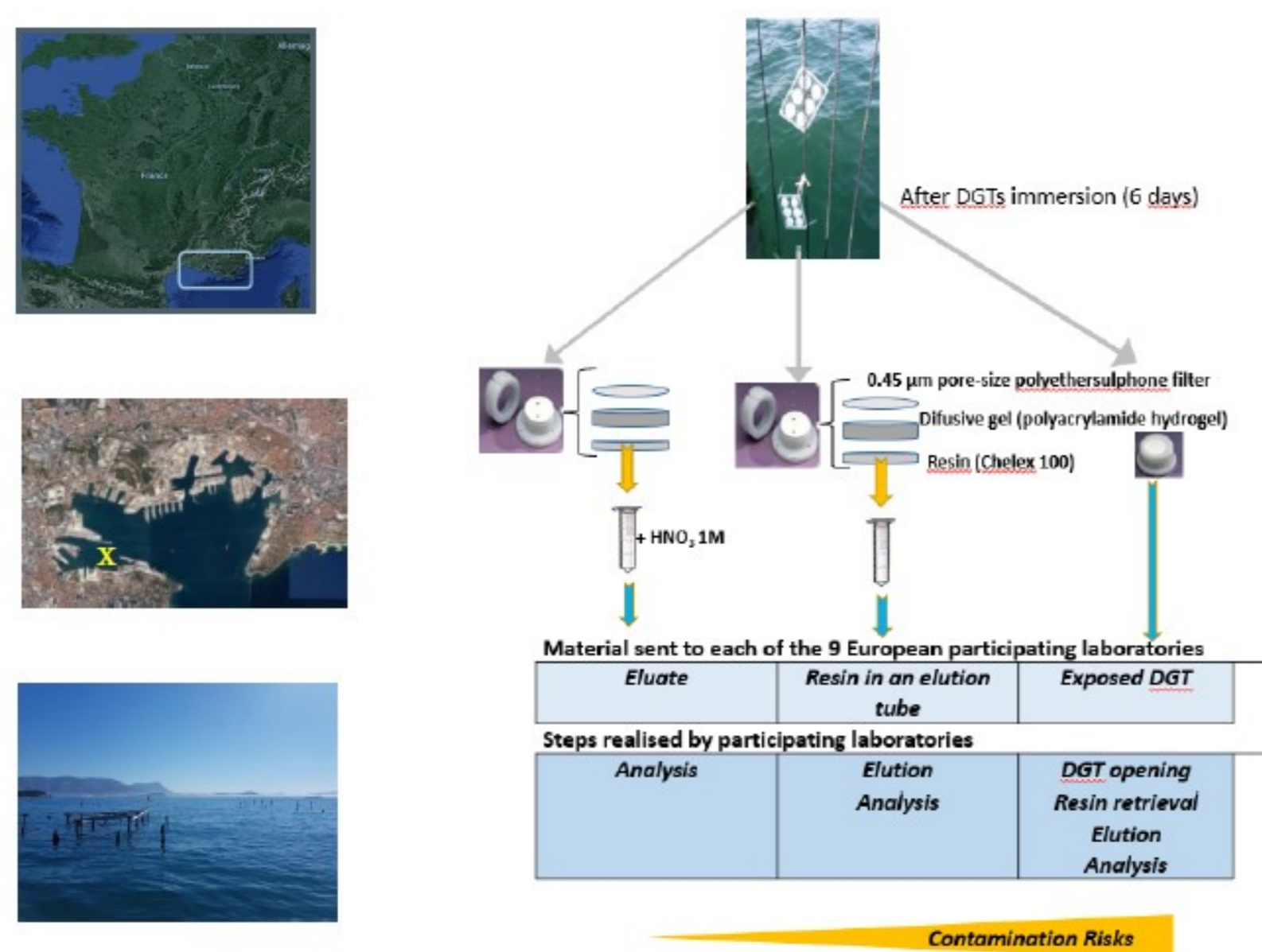


Figure 1 – DGT handling steps for each supplied material.

## Highlights

- ILC European exercise focused on the use of DGT technique in the framework of WFD.
- Participation of nine expert laboratories of the Interreg MONITOOL consortium.
- The design of this ILC made it possible to compare the "step by step" performance of laboratories during the processing and analysis of DGT samples.
- Cd, Ni and Pb reproducible concentrations were obtained by the majority of laboratories.
- DGT sample analysis can be performed satisfactorily by laboratories experienced in measuring concentrations of metals at trace level in marine environments. Blank values should be used as systematic quality controls to be checked for the three studied metals.

## Reference

Jean-Louis Gonzalez, Isabelle Amouroux, Stephane Guesdon, Florence Menet-Nédélec, Emmanuel Ponzevera, Natalia Montero, Barbara Marras, Marco Schintu, Miguel Caetano, Margarida Correia Dos Santos, Marta Rodrigo Sanz, Vanessa Millán Gabet, German Rodriguez Jose, María Jesús Belzunce-Segarra, Joana Larreta, Iratxe Menchaca, Philippe Bersuder, Thi Bolam, Fiona Regan, Blánaid White, Hao Zhang, An international intercomparison exercise on passive samplers (DGT) for monitoring metals in marine waters under a regulatory context, Science of The Total Environment, 2022, 157499, ISSN 0048-9697, <https://doi.org/10.1016/j.scitotenv.2022.157499>

## Results

Figure 2 : Results for Cd, Ni and Pb (mass in ng). X-axis : participating laboratories anonymously represented by a number. The number shown inside the markers indicates the number of replicates used by the laboratory for analysis. Two dots for one lab indicates the use of "reserve" DGT devices. The last three bottom plots show mass results (in ng) measured in blank DGTs (dot outside the graph : the mean value of Ni measured by laboratory 7 in the reserve DGTs is 161.5 ng with a standard deviation of 140%)

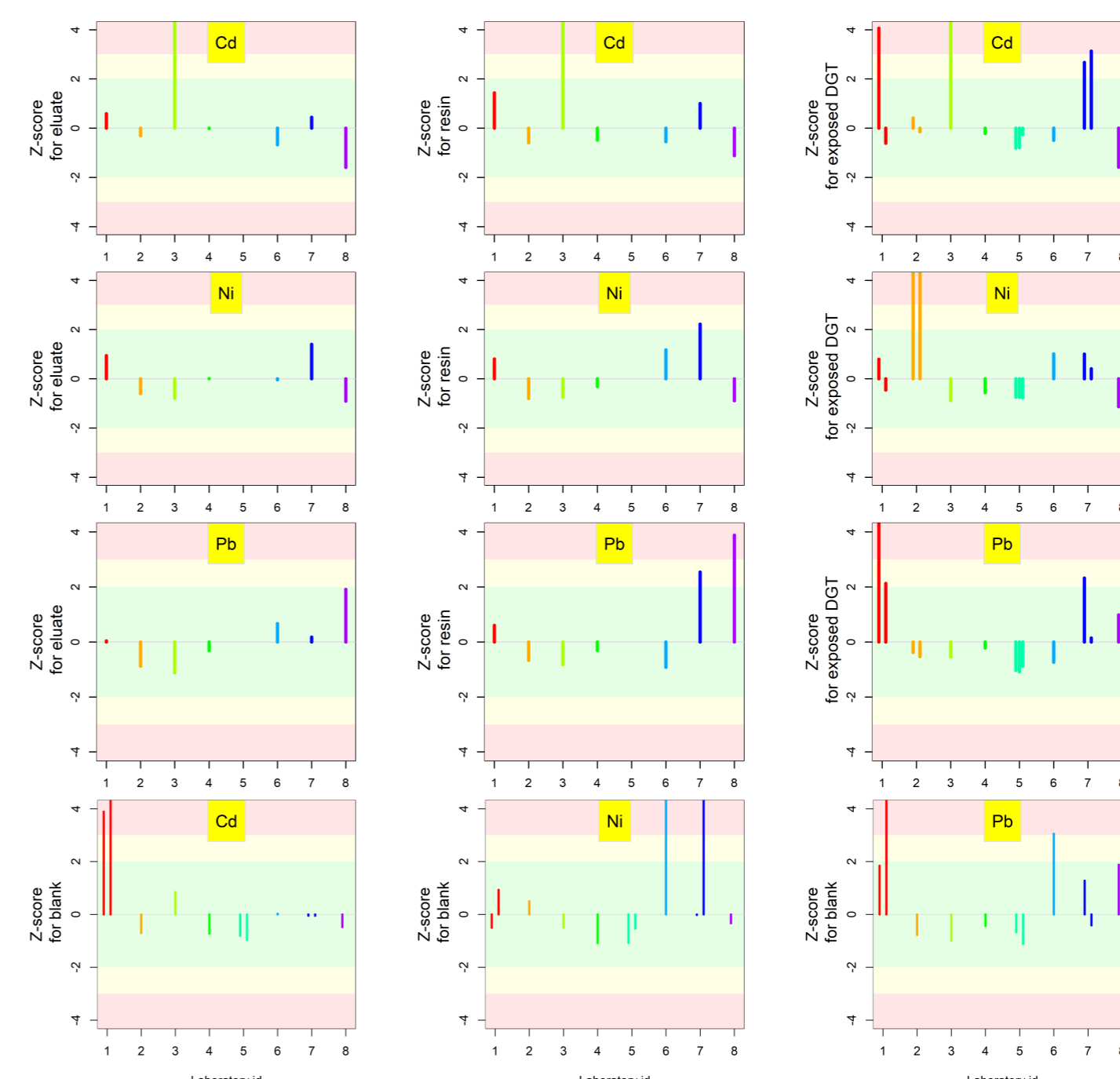
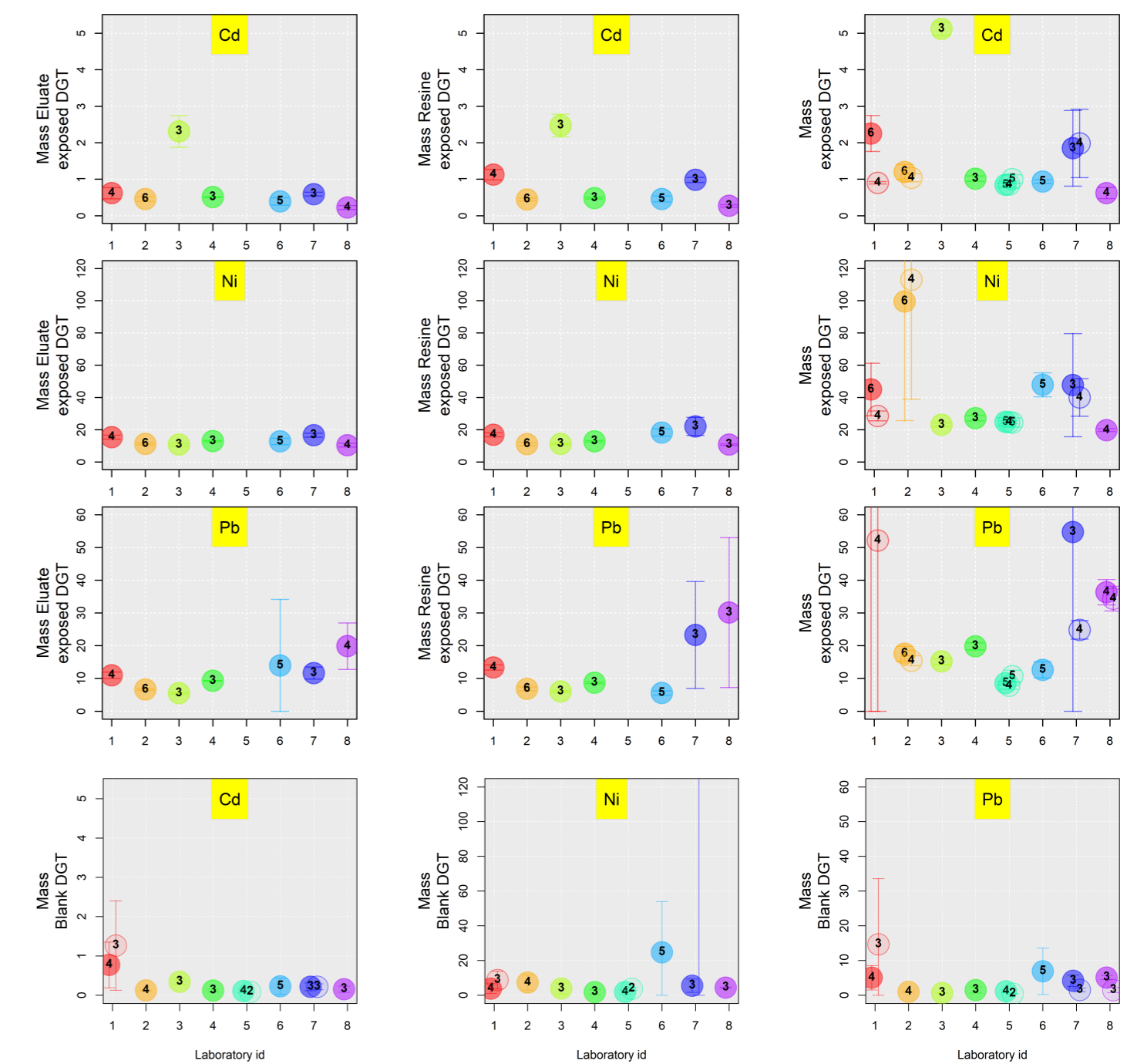


Figure 3 : Participating laboratories Z-Scores for Cd, Ni and Pb (X-axis : participating laboratories anonymously represented by a number). The last three bottom plots show blank DGTs Z-scores.

Table 1 – Z-score results obtained at each step of the analytical process.

	Eluate	Resin	Exposed.DGT
Satisfactory results	6 (Cd) 7 (Ni) 7 (Pb)	6 (Cd) 6(Ni) 5 (Pb)	9 (Cd) 11 (Ni) 11 (Pb)
Questionable results		1 (Ni) 1(Pb)	1 (Cd) 2 (Pb)
Unsatisfactory results	1 (Cd)	1(Cd) 1 (Pb)	3 (Cd) 2 (Ni) 1 (Pb)
Proportion of satisfactory results among all analysis results	95%	81%	77%

## Main conclusions

- Regarding blanks, the majority of laboratories performed adequately even at low Cd, Ni and Pb concentrations and measured values only represented a small part of the mass accumulated in deployed DGTs, enabling their use for reducing the uncertainties associated to potential contamination episodes. The ILC showed that blank values should be used as systematic "quality controls" to be checked for the three studied metals (Cd, Ni, Pb).
- Most of the unsatisfactory or questionable results (9/14) concerned the "exposed DGT", suggesting that DGT-handling and retrieval of the resin gels can be important sources of contamination if not performed carefully. These critical steps must be optimized to reduce contamination sources (e.g. by using Teflon coated tools for DGT opening and resin gel recovery, wearing protective sleeves above lab coat cuffs, improving clean bench air circulation, avoiding underflow hand positions, reducing manipulation time).