



ORIENTAMENTO CONSAPEVOLE

23 Aprile 2024

- DIPARTIMENTO DI CHIMICA -

La Chimica nelle Scienze Forensi.

Casi studio.

Lorena C. Giannossa

lorenacarla.giannossa@uniba.it



**UNIVERSITÀ
DEGLI STUDI DI BARI
ALDO MORO**



COSA SONO LE
SCIENZE FORENSI?



COSA SONO LE SCIENZE FORENSI?

Tecniche e metodologie scientifiche applicate alle tradizionali investigazioni di carattere giudiziario, in relazione all'accertamento di un reato o ad un comportamento sociale.



Scienze
Forensi

- ❑ Chimica
- ❑ Biologia
- ❑ Fisica
- ❑ Geologia
- ❑ Medicina
- ❑ Informatica
- ❑ Psicologia e Psichiatria
- ❑ Ecc.



Scienze
Forensi



Cos'è la chimica forense?

- è l'applicazione di principi scientifici e di analisi chimiche volta alla risoluzione di questioni legali
- uso di tecniche chimiche per identificare e/o quantificare tracce di sostanze note o sconosciute per tracciare la loro origine ai fini di un'indagine legale
- è soprattutto la **CHIMICA ANALITICA APPLICATA** e ciò che la distingue è la scienza del confronto





- **LA CHIMICA ANALITICA È LA BRANCA DELLA CHIMICA CHE COPRE LE ATTIVITÀ VOLTE ALL'IDENTIFICAZIONE, ALLA CARATTERIZZAZIONE CHIMICO-FISICA E ALLA DETERMINAZIONE QUALITATIVA E QUANTITATIVA DEI COMPONENTI DI UN DETERMINATO CAMPIONE.**



Cosa fa il chimico forense?

Quando il chimico forense lavora su un reperto, generalmente è chiamato a svolgere tre compiti:

- **IDENTIFICAZIONE** (analisi qualitative e quantitative)
- **CLASSIFICAZIONE** (colore, morfologia, ecc.)
- **INDIVIDUAZIONE DI UNA POSSIBILE ORIGINE**



Il quesito forense **non** è lo stesso di quello legale:

- Quesito forense:
«Questa polvere bianca contiene uno stupefacente? Se sì, quanto?»
- Quesito legale:
«L'imputato è colpevole di possesso di stupefacenti?»

Il chimico forense fornisce dati che possono contribuire a rispondere al quesito legale, all'interno di un quadro di indagine complessivo.





La chimica analitica fornisce dati qualitativi e quantitativi necessari alla domanda forense, per esempio;

- Da dove potrebbe venire questa fibra?
- Questo pezzo di plastica può provenire da quel sacchetto?
- Per appiccare questo incendio è stato utilizzato del gasolio?
- Questo frammento proviene da quella macchina?
- Il tipo di sostanza e la sua quantità trovata in campioni post mortem permette di risalire alla causa del decesso?



CHIMICA ANALITICA FORENSE



INTRODUZIONE ALLE SCIENZE FORENSI

LA CHIMICA ANALITICA NELLE SCIENZE FORENSI

- Principi, Applicazioni, Limiti.

CAMPIONE E CAMPIONAMENTO

- Problematiche e metodologie di campionamento, metodi di conservazione e trasporto del campione.
- Metodi di acquisizione e conservazione del reperto nel processo penale: sopralluogo tecnico, descrizione scena del crimine, fissazione e conservazione reperti, compilazione verbale.

TECNICHE DI ANALISI

- Criteri di scelta del metodo analitico, acquisizione del dato chimico, criteri di valutazione della significatività dei risultati.
- Tecniche spettroscopiche applicate alle indagini forensi (Raman, UV - Visibile, IR, esempi di applicazione)
- Tecniche microscopiche applicate alle indagini forensi (MO, SEM, esempi di applicazione)
- Tecniche cromatografiche applicate alle indagini forensi (LC, GC, GCMS, esempi di applicazione)
- Rilevamento delle impronte digitali su superfici porose e non porose: tecniche ottiche, chimico-fisiche e radioattive, AFIS (Sistema Automatizzato di Identificazione delle Impronte).



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ANALISI DI ESPLOSIVI

- Analisi esplosivi integri e residui di esplosione.
- Ricerca di sostanze acceleranti la combustione e di loro residui.
- Cenni di balistica forense (residui da sparo)

AUTENTICAZIONE DI BENI CULTURALI

- Le categorie del falso
- Tecniche per l'autenticazione

CAMPIONI BIOLOGICI (cenni)

- Accertamenti biologici indicativi: Luminol, test TMD, luce UV

SOSTANZE TOSSICHE/VELENI

- Veleni nella storia
- Classificazione
- Inorganici e Biologici. Iponatriemia. Tossine.
- Misurazione della tossicità

SOSTANZE PSICOTROPE E STUPEFACENTI

- Modalità di Classificazione
- Droghe legali ed illegali
- Test e Analisi

ARMI NON CONVENZIONALI O DI DISTRUZIONE DI MASSA

- Biologiche, Chimiche, Radiologiche e Nucleari

ANALISI SU MATERIALI (FIBRE, TERRENI, VERNICI, ECC.)



CASO STUDIO



È la dose
che fa
il veleno





Veleno:

sostanza che, assunta da un organismo vivente, ha effetti dannosi temporanei o permanenti, fino ad essere letali, attraverso un meccanismo di tipo chimico.

Tossicologia:

disciplina scientifica che studia i veleni e la loro azione.

Antidoto:

sostanza in grado di contrastare una forma di avvelenamento



Intossicazione:

stato patologico dell'organismo causato dall'azione di una sostanza esogena o endogena, tossica per natura o dosaggio.

Questo stato anormale può essere causato

- da un veleno o qualunque altra sostanza tossica,
- da una quantità esagerata di alcool ingerita;
- da cibo contenente batteri o virus.

A seconda della **durata**, l'intossicazione può essere:

- acuta (breve ma intensa)
- cronica



L'avvelenamento può avvenire per via

- alimentare
- respiratoria
- cutanea



Contents lists available at [ScienceDirect](#)

Legal Medicine

journal homepage: www.elsevier.com/locate/legalmed



Case Report

Thallium toxicity due to adulterated infusion with thallium sulfate in eight members belonging to the same family nucleus: Autopsy findings and ICP-MS analysis (inductively coupled plasma mass spectrometry) in a triple homicide



Domenico Di Candia¹, Enrico Muccino³, Alessio Battistini², Michele Boracchi⁴,
Guendalina Gentile⁵, Riccardo Zoja^{6,*}

Laboratorio di Istopatologia Forense e Microbiologia Medico Legale, Sezione di Medicina Legale e delle Assicurazioni, Dipartimento di Scienze Biomediche per la Salute, Università degli Studi di Milano, Via Luigi Mangiagalli, 37, 20133 Milano, Italy



1. Introduction

Among all the different intoxications caused by heavy metals, those caused by thallium (Tl) are still quite significant but can be usually enlisted as accidental or professional events [1], suicide attempts [2] and rare voluntary adulterations of food [3] with homicidal purposes [4–6]. The authors of these homicidal events take advantage of the high toxicity of this poison and its characteristics, being this substance colourless, tasteless, odourless and challenging both the clinician and the forensic pathologist in a difficult diagnosis that requires several investigations and a solid expertise.

The Authors, in the following manuscript, are reporting the data concerning an exceptional, unique case of homicidal thallium poisoning occurred in Italy and involving 8 members of the same family nucleus, three of which deceased because of voluntary adulteration of a herbal infusion, poisoned with thallium sulphate by another member of the family, grandson of the victims. Single cases are discussed and the results of the toxicological-forensic analysis, fundamental in the outlining of the homicide event, assessed with ICP-MS, are reported (Table 1).



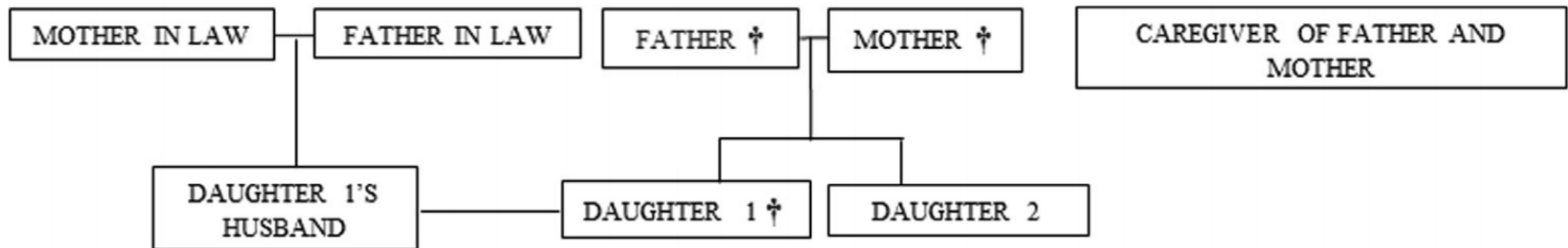
- incolore
- inodore
- insapore
- intossicazione di 8 membri dello stesso nucleo familiare
- adulterazione volontaria di un infuso a base di erbe



The following day five other members of the same family showed the same symptoms of the first three patients and the formulated diagnosis was identical.

Crime scene investigations were assessed on several houses belonging to the family and 70 specimens, environmental samples and food samples, among which an unlabeled infusion, were analyzed. According to the investigations carried out, a high dosage of thallium sulphate was detected in the same infusion that was regularly drunk by the whole family every afternoon. In fact, all the family members that drank the infusion had manifested the same symptoms and since the intoxication involved all the members of a specific family it was inferred that the poisoning was assessed with homicidal intentions.

- AUMENTO NUMERO DI INTOSSICATI
- STESSA SINTOMATOLOGIA
- SOPRALLUOGO CAMPIONAMENTO DI 70 REPERTI
- RITROVAMENTO DEL TALLIO SOLFATO
- IPOTESI DI OMICIDIO





3. Autopsy investigations

3.1. External examination

The corpses appeared to be in overall good conditions of preservation. A few signs of injections

3.2. Internal examination

From all the corpses, during autopsy examination, an extensive sampling of all the biological matrices was assessed in order to carry out chemical-toxicological analysis.

At autopsy examination, for the three victims, no other lethal cause of death could be determined and the *exitus* could be ascribed to respiratory failure in a context of suspected intoxication for the father and for the oldest daughter and the mother, the cause of death was identified in multi-organ failure in a context of suspected acute intoxication from thallium.

- CAMPIONAMENTO DI MATRICI BIOLOGICHE

- CAUSA DELLA MORTE:

COLLASSO MULTI-ORGANICO IN UN CONTESTO DI SOSPETTA INTOSSICAZIONE ACUTA DA TALLIO



4. Toxicological-forensic investigations

In order to confirm the episode of thallium poisoning, already detected with *intra-vitam* analysis assessed during hospitalization, we proceeded with toxicological post-mortem investigations on biological matrices sampled during the autopsy examination of the three corpses.

Toxicological screening was assessed following the Bureau of Legal Medicine of the University of Milan's standard procedures and we assessed a targeted research of the most common substances of abuse.

Psychoactive drugs (cocaine, amphetamines, ecstasy, methadone, opioids and ketamine) were screened with immune-enzymatic analysis (ELISA) using a Dinex instrument and analyzing femoral blood, cardiac blood and a liver specimen. The three victims did not show positivity for these molecules. BAC (Blood Alcohol Content) assessed with gas chromatography and HPB-Alc column with head-space technique in order to detect a qualitative-quantitative value of ethylic alcohol in femoral blood; all victims resulted to be negative. Organic volatile substances screened with gas chromatography with CP Sil 8MS/LB column. All victims resulted to be negative for these substances.

- ANALISI POST MORTEM PER CONFERMARE LA MORTE PER AVVELENAMENTO
- SCREENING TOSSICOLOGICO PER ESCLUDERE PRESENZA SOSTANZE PSICO-ATTIVE
- TEST QUALI/QUANTITATIVO PER PRESENZA DI ETANOLO



In order to better target the research for metals, since *intra-vitam* exams showed a severe thallium toxicosis, we proceeded with a quantitative evaluation of thallium via ICP-MS analysis on several biological matrices sampled during autopsy examination.

For the preparation of the samples in order to assess ICP-MS analysis, 0.5 mL of femoral blood, 0.5 mL urine and 0.5 mL of gastric content were digested according to EPA DG-CL-03 standard procedures. Nitric acid (HNO_3 , 69% Hiperpur Solution) and hydrogen peroxide (H_2O_2 , 30% Hiperpur Solution) were purchased from Panreac Quimica SLU (Castellar del Valles, Barcelona, Spain). Purified water was obtained through a Milli-Q system (Millipore, Merck KGaA, Darmstadt, Germany). Together with these samples, we proceeded with the digestion of the calibration points as well, prepared with appropriate dilutions of an Agilent standard thallium in an aqueous solution of 5% HNO_3 . Each sample was mineralized according to the previously cited EPA digestion method.

- ANALISI QUANTITATIVA VIA ICP-MS



- PREPARAZIONE DEI CAMPIONI

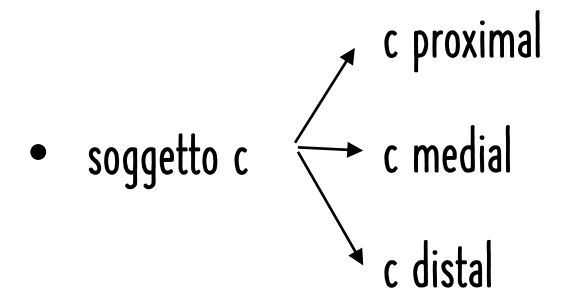
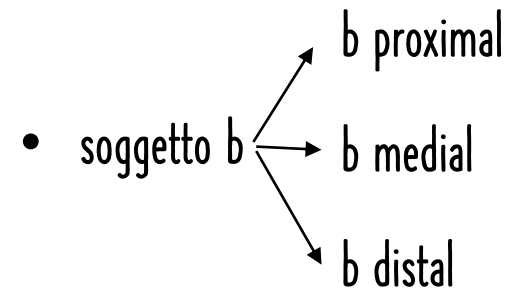
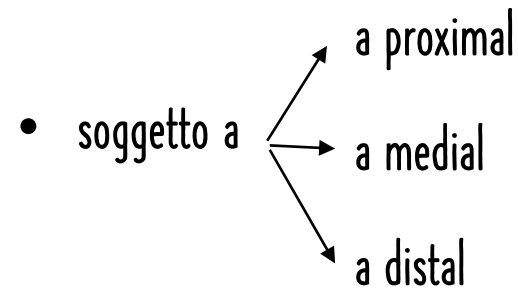
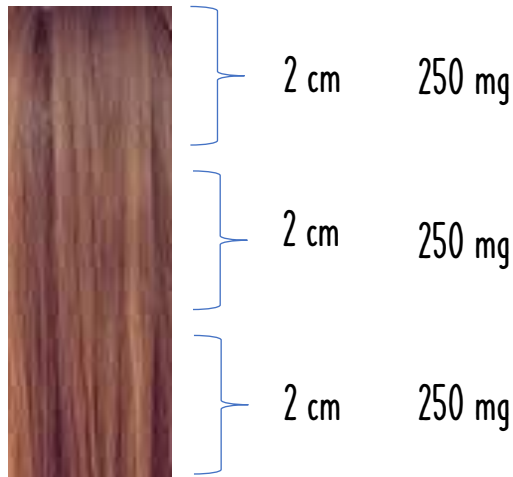
- DIGESTORE A MICROONDE





For the preparation of the **hair samples**, a hair lock from each cadaver was segmented into three different sections each: **a sample was composed by the proximal 2 cm of hair, the second sample was composed by the medial 2 cm of hair and the third sample was composed by the 2 distal centimeters of hair.** **250 mg of each of the 9 hair samples was then digested according to EPA DG-CL-10 standard procedures.** A

- CAMPIONI DI CAPELLI





The **high concentrations of thallium** detected in the biological matrices concerning the three victims (Table 1), **much higher compared to doses already considered as lethal under a toxicological point of view, evaluated in a range between 0.5 and 11 mcg/mL, were considered as coherent with the clinical presentation of the intoxication and the diagnosis was evaluated to be of an acute intoxication of the metal, orally administered and responsible for their death.**

The Judicial Authority did not allow the analysis on biological samples collected from the survived five members of the family nor the divulgation of the analytical results obtained during hospitalization of the patients.

- DL50 0.5-11 $\mu\text{g}/\text{mL}$
- L'Autorità giudiziaria non ha permesso che venissero repertati campioni biologici sui sopravvissuti né che venissero divulgati i risultati analitici ottenuti durante la degenza.

Victim	Matrix	Thallium dosing at hospital	Survival time	Post-mortem thallium dosing with ICP-MS
Father	Blood	3.40 mcg/mL	2 days	2.75 mcg/mL
	Urine	22.00 mcg/mL		1.49 mcg/mL
	Gastric content	/		1.93 mcg/mL
	Hair	/		10.11 ng/mg
Daughter 1	Blood	10.00 mcg/mL	2 days	6.01 mcg/mL
	Urine	42.00 mcg/mL		/
	Gastric content	/		3.43 mcg/mL
	Hair	/		5.72 ng/mg
Mother	Blood	5.70 mcg/mL	14 days	1.15 mcg/mL
	Urine	16.30 mcg/mL		/
	Gastric content	/		1.11 mcg/mL
	Hair	/		10.38 ng/mg

Table 1
Thallium concentrations detected in the victims during hospitalization and at toxicological-forensic exam.



Discussions

In the cases treated in this work, the demonstration of high concentrations of thallium in biological matrices (cardiac blood, urine, gastric content and hair) sampled from the three victims during autopsy examination, was assessed with a very sensible analytical technique for detecting the presence of these trace elements and able of measuring ppq (part-per-quadrillion) quantities in solution: the ICP-MS [25]. Hair samples were taken from the occipital area of the scalp, according to the Italian Healthcare Minister's guidelines, since this region is richly vascularized granting a more reliable distribution of substances of toxicological interest in this matrix. The presence of thallium in the first 2 cm of hair analyzed with ICP-MS technique, and the absence of the element in the remaining 4 distal centimeters, was in accordance with the several attempted adulterations put in place by the indicted and confessed during interrogation by the police. The concentrations of thallium in the distal 4 cm of hair were lower than 0.02 ng/mg and so to be considered of no toxicological interest: the negativity of the distal end of the hair locks underlined that the homicide attempts had started no more than two months before the effective death of the three relatives of the murderer.

The evidence of autopsy investigations, together with toxicological analysis, thanks to the aid provided by this sensible and specific technique, demonstrated the presence of high concentrations of thallium in the biological material examined, and was of fundamental help in building up the accuse of lethal thallium-toxicity in the analyzed cases.

- campioni di capelli suddivisi in sezioni: tallio presente nei primi 2 cm e non negli ultimi 4 cm
- tentativi di avvelenamento iniziati non più di 2 mesi prima dei fatti
- contributo sostanziale della tecnica analitica per l'impianto accusatorio



Police investigations

After two months of investigations, Police agents found a non-deleted e-mail on the computer of a 27-year-old grandson of the elderly couple, son of the younger daughter. The e-mail concerned a solicit for the delivery of 6 flacons of thallium sulphate for a total weight of 60 g ordered in June. The Inquiring Authority detected, moreover, a series of phone calls in which the suspect contacted a Paduan industry specialized in the commerce of thallium.

The unemployed accountant was enrolled in a Jews sect since 3 years before called Second Vatican Council and, following the *hiki-komori* rules (a Japanese word meaning “being confined”), voluntarily lived isolated from the external world and social life, spending his days using his personal computer.

Interrogated by the law enforcement agents, he confessed he had attempted to adulterate several times the infusion his mother was used to prepare every afternoon and serve to her old parents and other family members, all reunited to drink it, with thallium sulphate in order to estimate the proper dose to cause the death of his relatives. According to his confession, the motivation for such an act was that he considered his family “guilty of being impure” and “too attached to material goods”.

- confessione, accusa e sentenza

- mail

- setta

The young man was therefore arrested and accused of triple first-degree murder and quintuple attempted murder but he was then found not guilty due to complete mental illness and sentenced to 10 years of judicial psychiatric hospital.

PODCAST



PODCAST

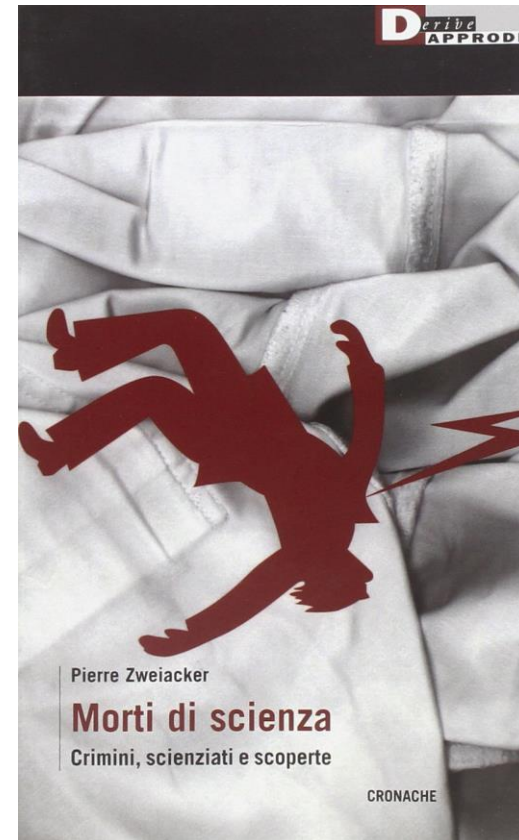
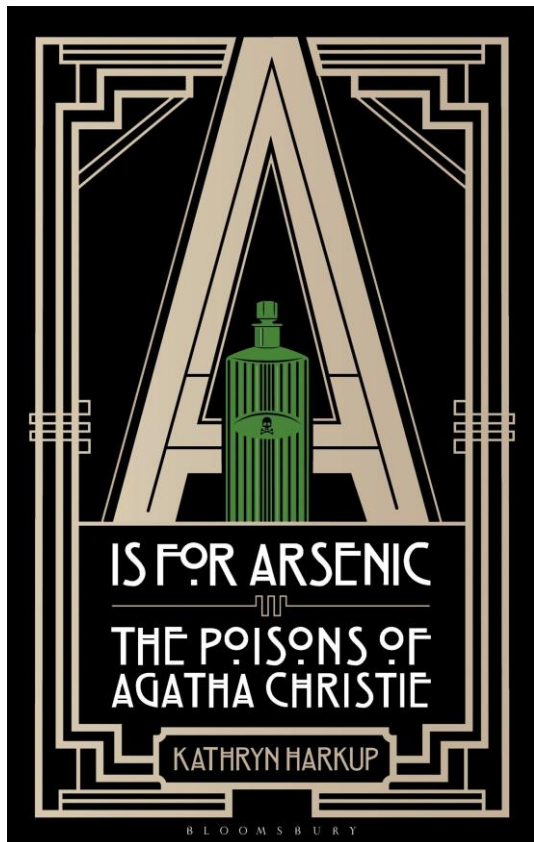


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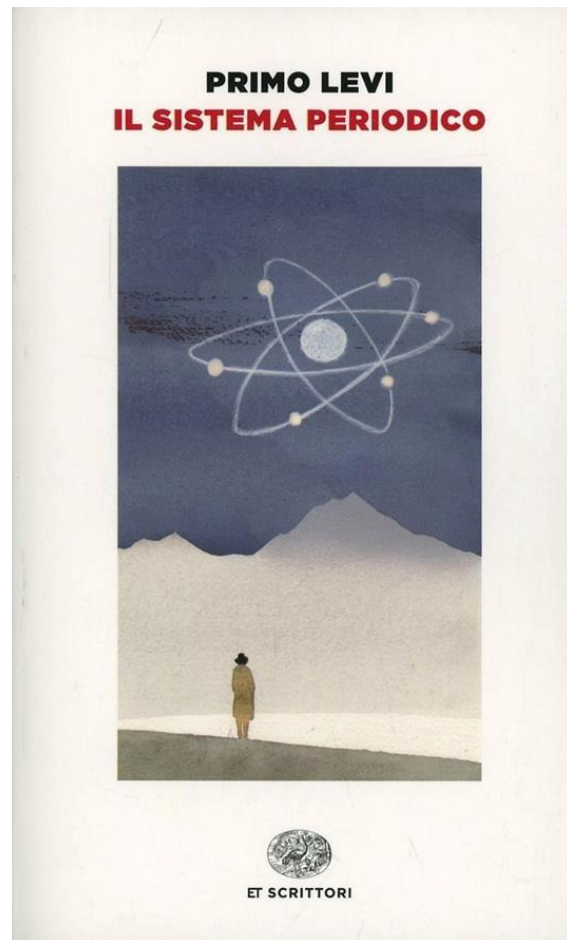


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